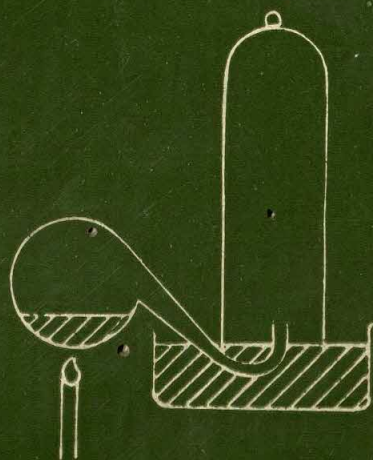# OXFORD
# MODERN SCIENCE

# 2

## CHEMISTRY

## John West

# OXFORD MODERN SCIENCE

## Volume 2

# CHEMISTRY

For Classes 7 & 8

**JOHN WEST**

*Head of Science*
*Mount Hermon School, Darjeeling*
*and Lecturer*
*M. H. College of Education, Darjeeling*

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John WEST

Illustrations by B. Pradhan

# Preface

In presenting this textbook of chemistry, the author is fully aware that what might be suitable and interesting to one teacher may not be so to another. However, a sincere attempt has been made to meet the needs of both teachers and students. It is the needs of students which are of paramount importance, and their active participation is essential if the best 'results are to be produced. By the 'best results', one does not necessarily mean results measured in terms of examination success, but rather that the students have opportunity to share in the excitement of chemistry and feel the rich pleasure that comes from discovery.

This does not mean the uncritical adoption of the 'discovery method', since this assumes that students approach the study of chemistry without any preconceptions at all, and that concepts and laws are to be learned slowly from the painstaking collection of facts at the bench. In this book, facts are given where necessary for the smooth progression from one topic to another. In experimental investigations the students are expected to take part in order to find out for themselves just exactly what happens. Experimental work is designed to give students experience and to stimulate their continued interest. In some cases, the way of discovery is mapped out by taking a historical approach to the subject. This is, of necessity, simplified and may give the impression of smooth progress until the final result was achieved. The students' own practical experiences should go a long way towards correcting this idea as they run into various snags and commit errors.

At the level of this first volume, knowledge of the intellectual growth of children and of their learning processes indicates that curiosity is one of the main driving forces of children. Thus the principal means of firing enthusiasm should be through invoking curiosity. The teaching of chemistry provides unique opportunities for this, since the teacher can constantly refer to the usefulness of the subject, and its relevance to life, which has the drama and magic of change but also the pattern and power of a well-ordered system.

The aim of this book is to make chemistry stimulating and relevant to present needs and interests. In addition, the method of teaching chemistry must give students first-hand experience of scientific methods. Also information must be given about what chemistry is doing and attempting to do today. Chemistry is not to be taught in isolation, and special emphasis must be given to the human aspects of scientific endeavour. To fulfil

these aims a great deal of fact and information has been given. These are often for reference and wider understanding, and are not intended for memorising by the student.

The chapter questions have been designed to ensure that the student has a correct understanding of the whole text, and will remember its essentials.

No preface is complete without a word of thanks and this is perhaps the most difficult part. Difficult, that is, in knowing where to begin because one could say that the start should be made with one's first teacher of chemistry over twenty years ago. Certainly he made chemistry stimulating by firing enthusiasm through curiosity. However, the list of names will be restricted to those immediately concerned in the preparation of this book. Thanks are due to Mr C. S. Rawat for the typing of the manuscript, to my wife Pauline for patient forbearance, for encouragement, for assistance and for the preparation of the index, and to Mr B. Pradhan for his excellent illustrations which so aptly capture the spirit and so accurately portray the fact of the text. A special word of thanks is due to the General Editor of this series, Mr Maurice Banerjei who spent many hours in careful consideration of the draft of each chapter before its final submission.

*Darjeeling 1973*                                                 JOHN WEST

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# Introduction

THIS book presents a two-year course in chemistry for Classes 7 and 8. It will be followed by a two-year course for Classes 9 and 10, and these two books will provide a complete course in chemistry for students taking a general education till a terminal stage in Class 10. The course leads particularly to the I.C.S.E. examination in Chemistry, but more generally it aims to provide the teacher and the student with a carefully planned course which contains all the chemistry that a student should know before ending a general education. If he or she later specializes in the Humanities, this knowledge of chemistry would lead to a broader and more vital understanding of the physical world. If the student later specializes in Science, this course will form an excellent foundation on which to build the future study of chemistry. In any event he or she will have had a valuable and enriching experience, for the treatment and presentation of the subject matter has been carefully planned to develop knowledge sequentially, to relate experience to theory, and to inform the student of the physical and social implications of the chemistry which touches daily existence.

This book embarks the student on a voyage of discovery. It is rich in examples of the power and scope of the human intellect, and tells of the great achievements of mankind in this department of learning. It arouses interest and develops a spirit of inquiry; it satisfies the student's natural curiosity. It builds a platform of understanding of the nature and composition of matter, on which future study can safely and surely rest.

*Darjeeling 1973*

MAURICE BANERJEI
*General Editor*

# Contents

# Part 1

FOR CLASS 7

# 1
# States of Matter
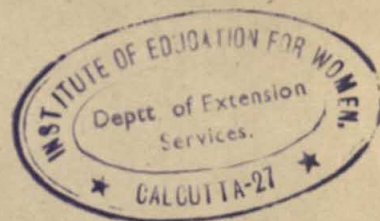
THERE is such a variety of materials existing on Earth, that the scientist looks for ways of arranging these materials into sets. This is known as classifying and a basis for classification is to find out how the materials behave. Another word used in place of material is substance, and the scientific word for materials or substances is *matter*. The ways in which matter behaves are known as the *properties of matter*.

All matter *has mass and occupies space*. Differences between one piece of matter and another may be in shape, mass, size, feel, colour, hardness, smell and so on. In this chapter matter is classified according to its *state*, that is to say, whether it is solid, liquid or gas (also referred to as the vapour state).

## 1. Solid, liquid and gas

What are the properties of solids, liquids and gases? How can these three states of matter be distinguished from each other? A look at the most common liquid matter on the Earth's surface — water, will help to answer these questions. If this liquid is cooled down, it becomes the solid known as ice. Heating the liquid changes it eventually into the gas known as steam. Usually steam is thought to be the white cloud seen near the spout of a kettle of boiling water. However, careful observation reveals a gap between the end of the spout and the white cloud. Steam, which is invisible, is in the gap and the white cloud consists of tiny drops of condensed steam, that is steam which has changed back into water because of the cooling effect of the surrounding air (Fig. 1.1).

To take liquid water from one place to another requires some kind of container. The liquid takes the shape of whatever container it is put into, but the amount of water remains the same. This is true of any liquid. Kerosene oil is stored in large drums at the agent's shop, and a litre of it has a very different shape from that which it has when run into a litre measuring can and when this litre is later put into the purchaser's bottle. These properties of a liquid are summarized by saying that the volume of a liquid is fixed but its shape is not.

Heat can be added to a liquid so that it changes state becoming a gas. Or, heat can be removed (this is known as cooling) and the liquid changes to the solid state. Solid water, that is ice, has a shape which is fixed unless an outside force such as a blow from a hammer causes it to take on the new shapes of the broken pieces. The fixed shape of solids is their particular

white cloud
(tiny drops of
water)

gap
(steam)

heat from stove
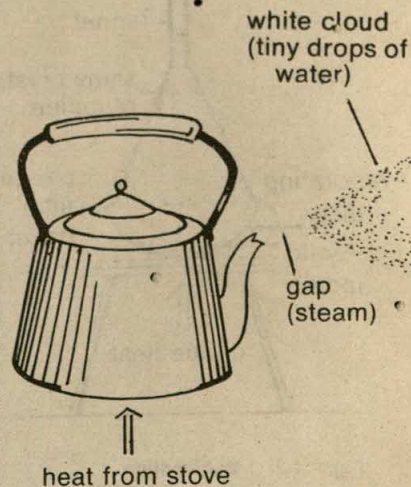
Fig. 1.1 **Steam is invisible**

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property and with the shape being fixed, the volume is also fixed. The fixed shape is due to the strong attraction between the particles making up the solid. This attraction is known as *cohesion* and is very strong in solids which keep the same shape unless changed by outside forces.

In complete contrast to a solid, a gas has neither fixed shape nor fixed volume. Gases have to be kept in closed containers, otherwise they will spread out to occupy all the space available. Experiments involving the handling of gases have to take into account this property. When gas jars are filled, they have to be closed with gas jar covers. If gas is obtained from cylinders then the valve must be closed when not in use. Care must be taken with the Kipp's apparatus used to generate hydrogen sulphide gas. If this gas is allowed to escape complaints will be voiced throughout the school as others become aware of the smell of rotten eggs. In a laboratory, all gas taps, to which no lighted Bunsen burners are fixed, must be kept closed. If this is not done, an inflammable and unpleasant smelling gas will spread throughout the laboratory. These are particular examples of the way gases behave in having no fixed shape and no fixed volume.

Starting with a solid and adding heat usually results in the formation of a liquid, and then with continued heating a gas is formed. Sometimes when a solid is heated it passes directly to the gas (or vapour) state. This occurs when iodine is gently heated as in Experiment 1.1.



funnel
shiny crystal of iodine
evaporating dish
pierced filter paper
solid iodine
gentle heat

Fig. 1.2 **Sublimation**
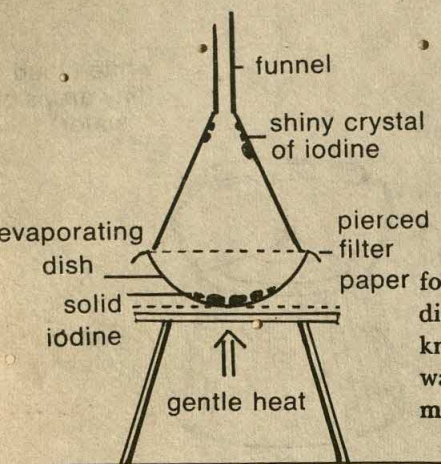
## EXPERIMENT 1.1

The apparatus is set up as shown in Fig. 1.2. When the dish is gently heated iodine vapour is seen to come from the solid. The vapour changes back into solid on the cold sides of the funnel.

This conversion of a solid directly into a vapour without melting, followed by condensation to a solid, is known as *sublimation*. Solid carbon dioxide also behaves in this way and because no liquid is formed, it is known as 'dry ice'. Dry ice is used for refrigeration purposes, since as it warms up, no liquid is left behind to be cleared away, or to spoil the material being kept cold.

## 2. Changes of state

Just as the term 'sublimation' is used to refer to a particular change of state, so there are terms for the other changes of state:

i) Solid to liquid is *fusion* or *melting* and the temperature at which it takes place is the melting point of the solid.

ii) Liquid to gas is *vaporisation* and this can take place at all temperatures, but above the boiling point the substance exists only in the gas state.

iii) Gas to liquid is *condensation* or *liquefaction*.

iv) Liquid to solid is *solidification*. In the case of water, this last change is usually called freezing and the temperature at which it takes place is the

freezing point of water. The freezing point of water is the same as the melting point of ice.

Fig. 1.3 shows the relationships between the states of matter and the changes occurring between these states.
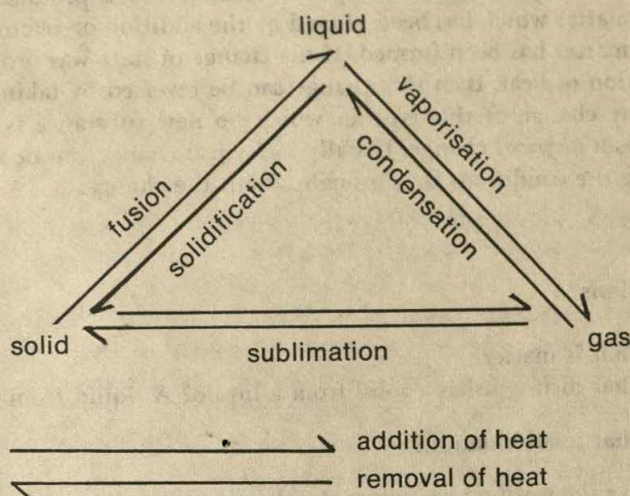


Fig. 1.3 **Interconversion of the States of Matter**

Water has been mentioned in this chapter because it is the only common substance seen in all three states. Other substances are ordinarily only encountered in one state. For example, rock is solid, petrol is liquid and air is gas. But in a volcano, rock melts and flows out as lava. Petrol can be solidified at about –60°C and has a boiling point around 120°C. Air is not easily liquefied and, as a result, the gases oxygen and nitrogen making up air are known as permanent gases. Although it is difficult to liquefy air, it is not impossible, and liquid oxygen and liquid nitrogen are available. This is most important because of the need of oxygen in steel making and of nitrogen for fertilizers. Even lower temperatures have been obtained and these liquids can become solid — solid oxygen has a melting point of –219°C and solid nitrogen –210°C. At the other end of the scale, we have solids which can only be converted into liquids with difficulty. Iron does not melt until its temperature is above 1500°C and its boiling point is 2800°C. To contain liquid iron as it is formed, something of even higher melting point must be used. This material is either calcium oxide with a melting point over 2500°C or magnesium oxide which melts at about 2800°C. These are known as *refractory* materials. Carbon, which we come across as diamonds in jewellery or the black rod in the centre of a torch cell, has a melting point over 3500°C.

Usually there is no difficulty in deciding the state of a substance, but doubtful cases do occur. Glass seems to be a solid, not changing its shape until a brick is thrown through a window, for example. However, in scientific works, statements such as 'glass is not a true solid, but is considered to be a super-cooled liquid' appear. Another similar situation occurs with pitch (asphalt) which is described in a dictionary of science as a semi-solid

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substance. An amusing substance is a new plastic material which flows very slowly but can be shattered by a hammer blow. It can be rolled into a ball and will bounce from a hard surface. If the ball is left on a table it gradually collapses into a puddle.

When a change of state takes place, nothing new is produced. It is the state of matter which has been altered by the addition or removal of heat; no new matter has been formed. If the change of state was brought about by addition of heat, then this change can be reversed by taking away the heat. Any change of this type in which no new substance is formed, is known as a *physical change*. Usually a physical change can be reversed by reversing the conditions that brought about the change.

## Questions

1   What is matter?
    What distinguishes a solid from a liquid? A liquid from a gas?

2   What is sublimation?

3   Give the word which names the change from solid to liquid, and the word which names the change from liquid to gas.

4   What features of a physical change can you discover from this chapter?

5   Under certain weather conditions snow gradually disappears without melting. What process is occurring?

6   What would be necessary to convert:
    a     oil into a vapour
    b     air into a liquid.

7   Name three substances you have met outside the laboratory which can be made to change state. Explain what has to be done to each to make it change state, and name the change of state concerned.

# 2
# Getting Pure Substances
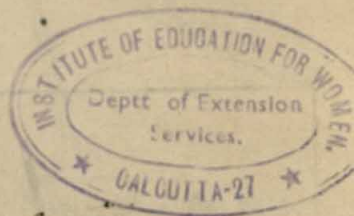
THE question that comes to mind at the beginning of this chapter is: 'What is a pure substance?' Closely related to this is the question 'How do we know that we have got a pure substance?'

The substances encountered in daily life are mostly mixtures of different pure substances. The atmosphere contains at least nine gases and where there is a lot of industry it is polluted by invisible smoke particles and gases issuing from the factory chimneys. Man also adds to the pollution of the atmosphere in other ways, with the fires he burns for cooking and warmth, the exhaust from his motor cars and from the aircraft which criss-cross the skies. The earth we tread upon contains hundreds of different substances which are taken out and made into many familiar materials. Water dissolves so many substances, that countless things make up sea-water. From all the mixtures that make up the substances occurring naturally, the chemist is concerned with taking out pure substances and studying their properties. But how can the chemist be sure that the extracted substances are pure?

Salt is a necessity in the lives of everyone. This is mainly the pure substance 'sodium chloride', but it is not pure; it contains very small amounts of other substances. Pure sodium chloride does not become damp if left exposed to the atmosphere. It is one of the impurities which is responsible for this. Different brands of salt will contain different impurities in differing amounts depending on the source and on the extraction process. This means that the salt will not always contain the same substances, nor will it always have the same properties. This is in contrast to pure sodium chloride, the composition and properties of which are fixed. For example, it always melts at the same temperature (800°C) and has the same density (2.20g/cm$^3$).

Another everyday example is steel. The chief pure substance in steel is iron, but it is mixed with carbon and other metals. Because steel is a mixture, it can be made with many different properties depending on what is put into the mixture and how much is put in. Some steels are stainless, some are magnetic, some are very hard; others do not have these properties. So, a varied composition causes a change in properties. But pure iron always has the same properties, its melting point is exactly 1535°C, and its density exactly 7.86 g/cm$^3$.

Thus it is possible to define a pure substance: *A pure substance has a fixed composition, and fixed properties, these being characteristic of the substance.*

Experiments 2.1, 2.2 and 2.3 are simple examples of the way in which properties of pure substances are altered by the presence of impurities. Experiments 2.1 and 2.2 make use of pure water — obtained in the laboratory or at a garage for filling car batteries as distilled water. Naphthalene is used in Experiment 2.3; this is one of the many substances obtained from coal.
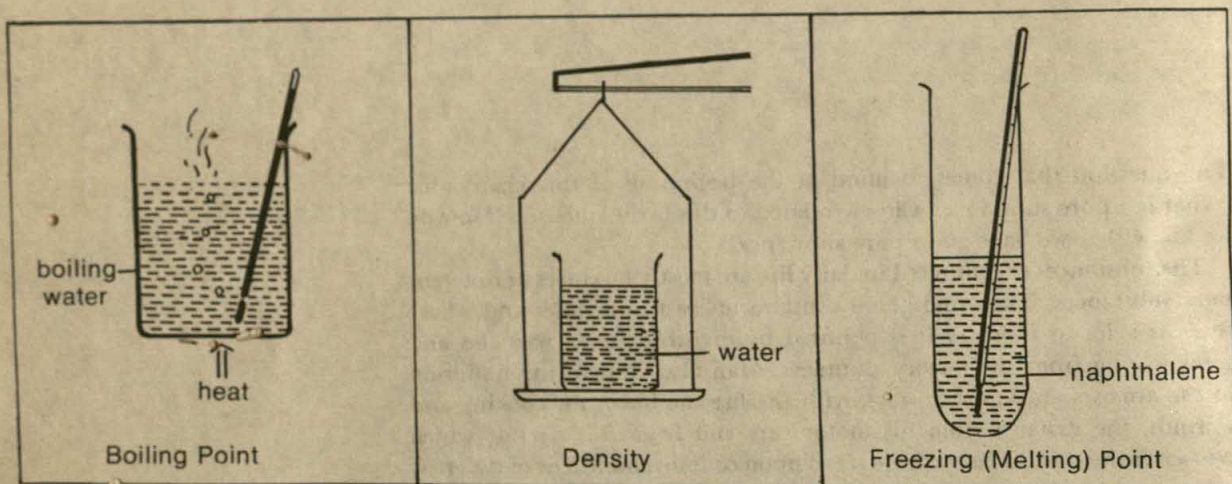


Fig. 2.1    **Using Physical Properties to Determine Purity**

## EXPERIMENT 2.1

Take a clean 100 ml beaker and half-fill it with pure water. Heat the beaker until the water begins to boil. Note the temperature with the bulb of the thermometer in the boiling water, but not touching the bottom of the beaker. Repeat this procedure, replacing the pure water with water containing salt. What has happened to the boiling point of the water which is now impure? Sample results obtained at the author's school in Darjeeling gave a 1°C rise in temperature with a solution containing 35 g salt in 100 g water.

## EXPERIMENT 2.2

1. Weigh a clean dry beaker and then pipette into it 25 cm³ (or 20 cm³), water. Find the mass of the beaker and water and hence the mass of 25 cm³ of pure water. From this information, the mass of 1 cm³ of pure water can be determined, that is, the density of water.
2. Repeat the experiment using salt water. Calculate the density of the salt water. In what way does this differ from the density of pure water? In measurements made using the same solution as above viz. 35 g salt/100 g water, 25 cm³ was found to be 0.79 g heavier than pure water.

## EXPERIMENT 2.3

Melt some pure naphthalene in a test tube and then allow it to cool, taking the temperature every minute. What do you notice? Does the

temperature fall all the time, or does it stay constant for any length of time? What is the freezing point (melting point) of pure naphthalene? In another test tube melt crude naphthalene (the word 'crude' is often used to describe an impure substance) and repeat the observations. What happens this time? Does the temperature fall all the while, or are there periods during which it stays constant?

The properties so far used to characterise pure substances are known as physical properties since they depend only on the substance itself and not on changing it into any new substance. Turning to the Chemistry section of a book such as Kaye and Laby, *Tables of Physical and Chemical Constants*, one finds several hundred substances listed together with their melting points, boiling points, and densities. These are of primary importance in identifying the purity of a substance. As your knowledge of Physics develops, you will find that there are other properties which can be used when the purity of a substance is questioned.

The questions 'What is a pure substance?' and 'How do we know that we have got a pure substance?' having been answered, it is now possible to look at the methods used for getting pure substances. How are pure substances separated from the other substances they are mixed with?

## 1. Filtration

Take rock salt as a starting point. Examination of rock salt, particularly with a hand lens, shows that mixed into the main body of the rock there are sand-like particles. This dirty rock salt is certainly not fit for the table; it must be cleaned in some way. Water is often used in cleaning but when water is added to rock salt in a clean test-tube, and this is shaken, it is not the sand which goes, but the salt. The salt *dissolves* in the water leaving the sand behind. The separation of the sand from the water containing dissolved salt is carried out by the process of *filtration* described in Experiment 2.4.



Fig. 2.2    Filtration

### EXPERIMENT 2.4

1. Set up a filter funnel as shown in Fig. 2.2 together with a filter paper cone.

2. Pour the liquid and solid from the test tube down a glass rod directed to the edge of the filter paper.

3. Observe that the liquid collecting in the beaker is clear and that the solid is left behind as a residue on the filter paper.

This only partly answers the problem. True, the sand has been removed, but pure salt has not been obtained. We have water in which salt has dissolved. Water is called the solvent and salt the solute and together they form a solution. There will be more said on this in Chapter 5. The problem now is 'How to separate the solute from the solvent?'
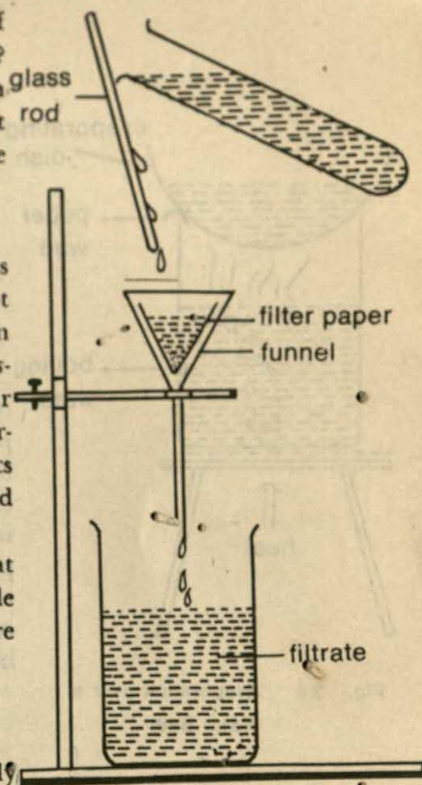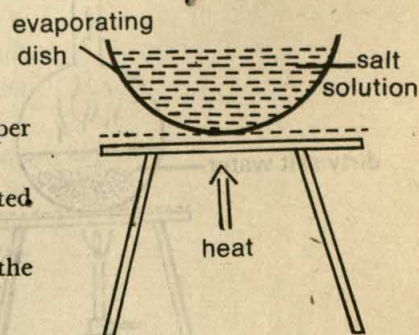


Fig. 2.3    Evaporation

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## 2. Evaporation

This separation is accomplished by driving off the solvent. Heating the solution causes the water to *evaporate* and the salt remains behind.

### EXPERIMENT 2.5

Pour the solution into an evaporating dish and place this on a tripod and gauze over a Bunsen burner. (See Fig. 2.3). In the later stages of the evaporation a small flame is necessary to avoid spitting. A slower rate of evaporation is obtained by using a water bath as shown in Fig. 2.4.

The product of Experiment 2.5 will be a white solid possibly consisting of large crystals if the later stages were carried out slowly. This is now a purer form of salt than the original rock salt. At this stage it is not possible to say whether or not it is the pure chemical substance known as sodium chloride. Supposing there had been some sugar mixed up with the rock salt at the beginning, then what would have happened? This is left as a problem for you, since both salt and sugar dissolve in water. It is necessary to realize that the white solid obtained at the end of Experiment 2.5, could contain other solids which are in the rock salt and which also dissolve in water.

Fig. 2.4    Evaporation over a Water Bath
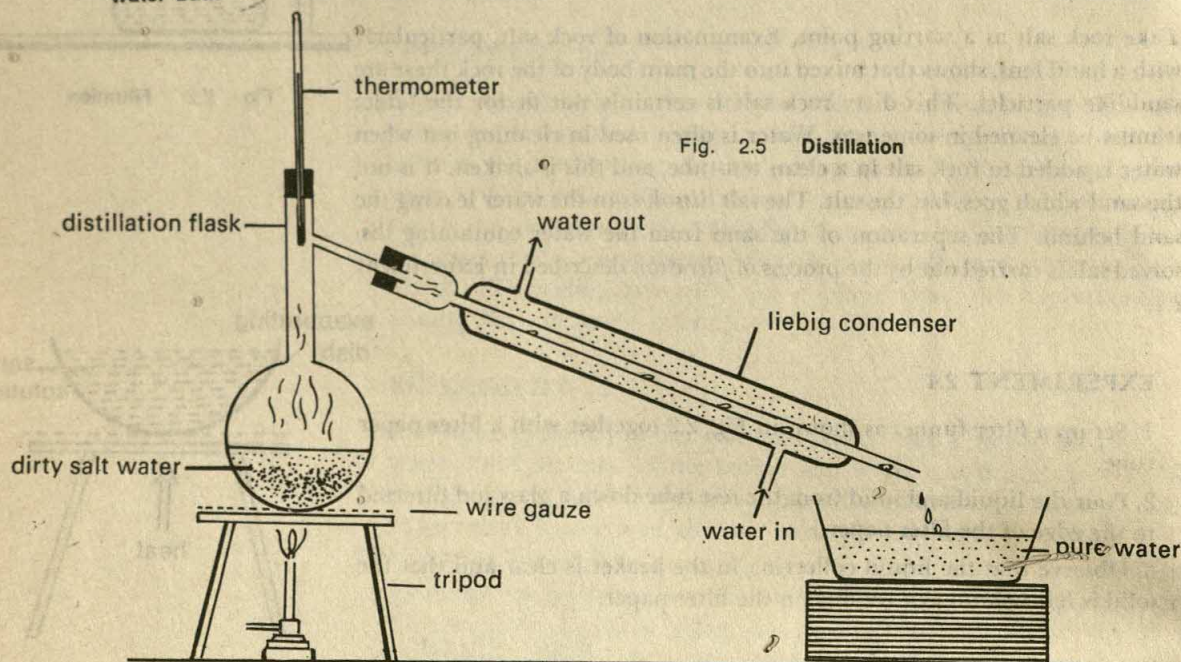
Fig.    2.5    **Distillation**

## 3. Distillation

The process of filtration followed by evaporation separates a soluble solid from an insoluble one and shows how the solute can be obtained from

a solution. If the solvent is required, *distillation* must be performed. A separation which is important and which will probably become more important is that in which pure water is obtained from sea-water. The laboratory procedure is described in Experiment 2.6.

## EXPERIMENT 2.6

1. The apparatus is set up as shown in Fig. 2.5. Note that the bulb of the thermometer is just below the side arm of the distillation flask. This records the temperature of the vapour passing into the condenser.

2. Cooling water enters the condenser through the lower inlet and leaves at the top so as to keep the condenser jacket full of cooling water.

3. A few small pieces of broken porcelain are placed in the distillation flask to ensure even boiling.

4. Put sea-water into the flask and heat it so that it boils. Water is collected from the end of the condenser. Take care that the flask is not boiled dry.

In a few places around the world, there are water distillation plants which provide the fresh water from sea water. In Kuwait, 36 million litres of fresh water are produced daily using heat from the burning of waste gas from local oilfields. In most countries the fuel for distillation plants is too expensive. It takes about 1 000 000 kg of coal to heat and evaporate enough sea water to equal one centimetre of rainfall on one square kilometre of land.

## 4. Decantation

Most water which is used in homes, factories and in other places, is collected from *surface water*. Rain water runs over the surface of the Earth and into various drainage systems leading to tanks, lakes, streams and rivers. Surface water usually has a lot of mud and dirt which have to be removed before the water can be used for the many purposes for which it is required. Water is collected in storage reservoirs where the large solid particles settle to the bottom. This process of settling called *sedimentation* can be speeded up by the addition of certain chemicals, for example, a mixture of alum and slaked lime. (Chemical names — potassium aluminium sulphate and calcium hydroxide respectively). Water is run off at the top of the sedimentation tank without disturbing the solid at the bottom. This is a large scale application of a process sometimes used in the laboratory known as *decantation*.

## EXPERIMENT 2.7

1. Put some lead carbonate into a test tube with some water, and shake vigorously. Stand the test tube in a rack. What happens?

2. Allow the solid to settle completely and then carefully pour off the water. This leaves the solid behind, which can be dried by gentle heating.

Decantation is used where a fairly dense solid is to be separated from a liquid in which it easily sinks. The water run off from the top of the sedimentation tanks is taken to filtration tanks to remove any solids which have not settled previously. Water is allowed to pass slowly through layers of sand and gravel and then into earthenware pipes (see Fig. 2.6) which carry the water away to the next stage of treatment, which will be considered later.



water
fine sand
coarse sand
gravel
earthenware pipes
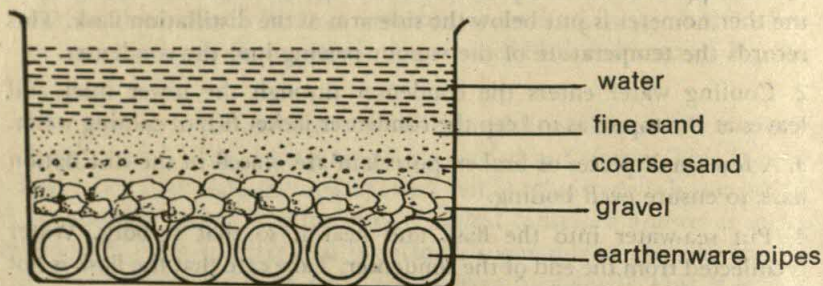
Fig. 2.6   A Filtration Tank

## 5. Chromatography

It has been shown that substances can be separated from one another by processes known as filtration, decantation, evaporation and distillation. These processes also have large scale applications, of which some examples have been given. Mixtures are separated in many other ways, some of which will be introduced later. This chapter concludes with a description of a separation method developed only over the last sixty years. Experiment 2.8 introduces the method.

### EXPERIMENT 2.8

1. Place a piece of filter paper (or blotting paper) on top of a beaker and put one drop of black ink in the centre. What happens?

2. Carefully put a drop of water at the centre of the ink blot and watch the blot spread out.

3. When the fast spreading slows down put another drop of water at the centre. This can be repeated if nothing special is seen, but after 3 drops of water, instead of a black colour, other colours should be seen in rings around the centre.

The actual results obtained in Experiment 2.8 will depend on the ink used, but the separation of the colour of the ink into different dyes should be seen. This method of separation is known as *chromatography*, since the people who discovered and used the method originally were concerned with separating coloured pigments. The actual discovery was made by a Russian chemist Tswett who in the first report of his work wrote of over 100 substances studied by chromatography. The pattern of separated colours is known as a *chromatogram*. There are many ways in which chromatograms can be produced. Experiment 2.9 describes another method.

## EXPERIMENT 2.9

1. Cut up a handful of grass (or spinach) into small pieces. Grind the pieces with acetone or methylated spirit in a mortar so that 2 to 3 cm$^3$ of green liquid can be decanted into a test tube.

2. Pour the green liquid into a small flat dish and stand a stick of blackboard chalk on end in it. Find out what you can about the colours that develop.

Despite the methods described for separating substances, it is very difficult to get one substance free from all other substances, that is 100% pure. For the chemist it is a constant problem to achieve purity in the substances used, since otherwise it is not possible to rely on the results of experiments. Distilled water has been referred to as pure water, but for experiments involving electrical measurements it is not pure enough and special methods have to be used to get super pure water. In the past a distillation apparatus made entirely of copper would have been used, but *ion-exchange resins* are now available (see Chapter 12).

In this chapter, the meaning of a pure substance has been set out together with some of the tests by which purity can be assessed. Since the title of the chapter is 'Getting Pure Substances', methods have been given by which pure substances can be obtained. It must be emphasized that these are only some of the simpler methods and others will find their place later in our study of Chemistry.

### Questions

1  What is a pure substance?

2  What effect does the presence of an impurity have on the boiling point of a liquid?

3  You are given a mixture of salt and charcoal. Describe the procedure by which you would obtain pure salt from this mixture.

4  Outline the stages by which water from a very muddy river could be made fit for drinking.

5  Explain what is meant by distillation. Draw a diagram of an apparatus by which a distillation could be performed. What is the purpose of carrying out a distillation?

6  What does the filtrate consist of when (*a*) salt solution, (*b*) muddy water, is filtered? What does the distillate consist of when sugar solution is distilled?

7  Iodine dissolves in chloroform. Describe how a mixture of iodine and sand could be separated (*a*) using chloroform, (*b*) without using chloroform.

(To answer part (*b*) you need to know something about iodine which you were told in Chapter 1).

# 3
# Elements and Compounds

CHAPTER 2 showed how to obtain pure substances by processes involving physical change. Having obtained the pure substance the physical processes can be continually repeated, but no further separation into different substances will take place. The pure salt obtained from rock salt can be re-dissolved in water, and the water evaporated, over and over again, but only salt will be left each time. It is however possible to melt salt and then pass an electric current through it, and this brings about an altogether different change in which a metal called sodium and a green poisonous gas called chlorine are obtained. The details of this process must wait till a later stage.

An electric current is used to break salt into other substances, and Experiments 3.1 and 3.2 show that heat will also *decompose* substances.

### EXPERIMENT 3.1

1. Place some lead nitrate in a test tube and heat gently. What do you hear? What do you see?

2. After a short while put a glowing splint into the test tube. (A splint is lit and then the flame blown out so that only the tip glows red-hot). What happens? What is the colour of the solid left behind?

Heating the lead nitrate has resulted in new substances being produced. The brown gas is nitrogen dioxide. The re-lighting of the glowing splint is due to the presence of oxygen, and the yellow solid left in the test tube is lead oxide. This change can be represented as follows:

$$\text{Lead nitrate} \xrightarrow{\text{heat}} \text{lead oxide} + \text{nitrogen dioxide} + \text{oxygen.}$$
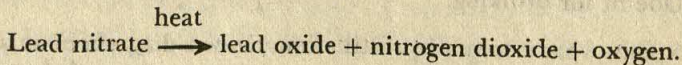
### EXPERIMENT 3.2

Put some mercury oxide into a test tube and heat. Note the change in colour. Test for the presence of oxygen as in Experiment 3.1. Observe the shiny appearance on the side of the test tube.

In this experiment, the mercury oxide has been decomposed by the heat into mercury and oxygen.

$$\text{Mercury oxide} \xrightarrow{\text{heat}} \text{mercury} + \text{oxygen.}$$
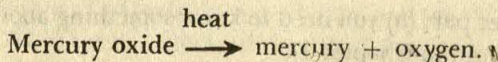
Since the process of breaking up pure substances has begun, the question now is, can it be continued? Is it possible to go on breaking up pure substances? Consider the products of Experiment 3.1. If lead oxide is placed on a charcoal block and heated in a blow pipe flame, as shown in Fig. 3.1, pure lead is obtained, the oxygen combining with the carbon of the block.



hole containing
lead oxide

blow pipe

carbon block

luminous flame.
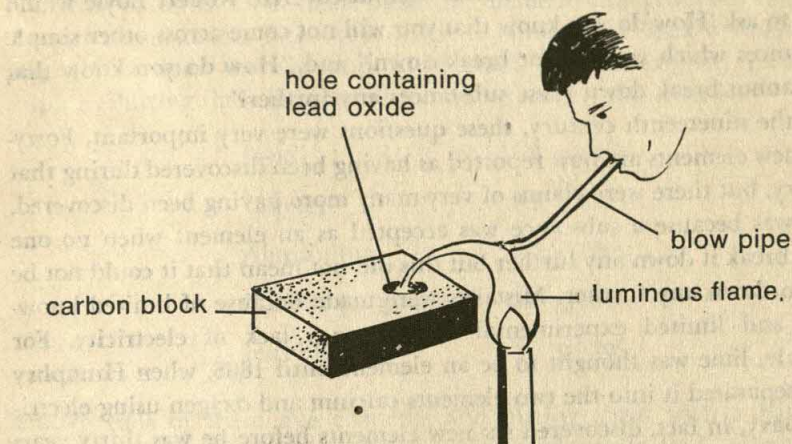
Fig. 3.1 **Using a blowpipe and charcoal block**

Nitrogen dioxide when passed over red-hot copper, gives up its oxygen to the copper, and nitrogen gas can be collected as the other product.

Copper + nitrogen dioxide $\longrightarrow$ copper oxide + nitrogen.

There are many changes which can be carried out in which pure substances are involved; some break down and others build up. In breaking down, a stage is reached where it is no longer possible to divide a substance any further. In the case of the experiments already carried out, this stage is reached when lead, nitrogen, oxygen and mercury are obtained.

So, pure substances can be divided into separate parts, but the process of division does not go on and on — there is a limit. Some pure substances cannot be further broken down. A pure substance which cannot be split up into anything else is known as an *element*. Robert Boyle (1627-1691) is responsible for this modern idea of an element. In 1661, he published a book entitled *The Sceptical Chemist* in which he suggested that an element should be thought of as a substance which could not be broken down further into other substances.

## 1. Discovery of elements

Following Boyle's suggestion, chemists began to search for these simple substances. Thirteen elements were known when Boyle wrote his book, although the term had not previously been applied to them. By the end of the eighteenth century another twenty had been discovered. In the nineteenth century forty-nine were added to the list. The total number of

elements known at present is one hundred and five. Of these, ninety-two can be found by breaking down naturally occurring substances. The other thirteen have appeared on the scene since 1940, having been made by scientists in their laboratories. Although it is possible that more man-made elements may be produced, we accept that all the elements that could be found in nature have now been discovered. Robert Boyle would want to ask 'How do you know that you will not come across other simple substances which you cannot break down?' and, 'How do you know that you cannot break down these substances any further?'

In the nineteenth century, these questions were very important. Forty-nine new elements are now reported as having been discovered during that century, but there were claims of very many more having been discovered. This was because a substance was accepted as an element when no one could break it down any further but this did not mean that it could not be broken down any further. Mistakes were made because of limited knowledge and limited experimental facilities e.g. lack of electricity. For example, lime was thought to be an element until 1808, when Humphry Davy separated it into the two elements calcium and oxygen using electricity. Davy, in fact, discovered six new elements before he was thirty years old. The great Swedish chemist Berzelius sometimes made mistakes. In 1815, he found a substance which he thought was a new element and he called it thorium. He discovered his own mistake a few years later when he was able to break the substance down into two elements which were already known — yttrium (discovered 1794) and phosphorus (discovered 1669). In 1829, he really did discover a new element which is the real thorium. There is a family of elements known as the 'platinum metals', and there are only six members of the family, but during the last century the discovery of fourteen more was reported! Lest the nineteenth century chemists be dismissed as incompetent, it should be remembered that they made lasting contributions to knowledge and also that they are not the only ones to have made mistakes. Only fifty years ago, it was claimed that a new element was discovered, but it turned out to be a mixture of titanium dioxide and iron oxide.

All this does not answer the questions 'How do you know that a substance is an element?' and 'Will we discover any more elements in nature?' Having posed the questions, the answer is going to be unsatisfactory because at this point the areas of investigation of chemistry and of physics overlap and the answer to the chemist's question is provided by methods used by the physicist. One method looks at the light which comes from a heated substance after it has passed through a prism. Each element has a unique pattern of light just as every human being has unique finger prints. These 'finger-prints' of the elements help us to distinguish one element from another. Also, although a chemist cannot split up an element, the physicist has been able to do so and we now know what makes an element and how it is different from any other element. This is as far as it is possible to go at this stage, but the matter will be considered again as this chemistry course develops.

## 2. Families of elements: metals and non-metals

As more and more elements were discovered it was felt that the study of elements would be made simpler if they could be put into families. Chemists felt that some pattern or patterns might exist so that the wide variety of elements could be put into a scheme which was orderly. A start in finding patterns can be made by sorting elements into groups or families. To sort the elements into their different families, we look at their properties. Consider the elements aluminium, carbon, copper, lead and sulphur. Putting these in order of decreasing density the order is:

| | |
|---|---|
| Lead | 11.3 g/cm$^3$ |
| Copper | 8.9 g/cm$^3$ |
| Aluminium | 2.7 g/cm$^3$ |
| Carbon (as graphite) | 2.3 g/cm$^3$ |
| Sulphur | 2.1 g/cm$^3$. |

Taking rods of these five elements and hitting them with a hammer, results in carbon and sulphur being shattered, while lead, copper and aluminium are just dented or flattened slightly. When the ability of these elements to conduct heat is measured, copper and aluminium are found to be very good conductors of heat, carbon and sulphur hardly conduct heat at all so they are known as heat insulators, and lead comes in between. A fourth property can also be considered, and that is the ability to conduct electricity. Copper, aluminium and lead are good conductors of electricity, sulphur is known as an electrical insulator and carbon in the form of graphite conducts electricity, but about half as well as lead which is in the first group. This information was, of course, first obtained through experiments; now it can be found in books of data. What should be done now is to use the information to sort the five elements into two groups. This is not very easy since there is no clear dividing line. Density would put lead and copper together having high density and then the other three elements would go together. Brittleness clearly puts sulphur and carbon in a separate group, so that aluminium moves from one group to the other. Aluminium and copper are definitely in the same group for conducting heat, and carbon and sulphur are separate from them with lead in between. Copper, aluminium and lead can be grouped together as good electrical conductors, sulphur is separate as an insulator, and carbon is in between. The usual grouping of these five elements is copper, aluminium and lead together as *metals* and carbon and sulphur as *non-metals*.

The following general statements can be made about metals: they have high density, they are good conductors of heat and electricity and they are not brittle. Non-metals have low density, they are not good conductors of heat and electricity and they are brittle. A careful study of the information already given shows that there are exceptions to these generalizations. e.g. the non-metal carbon can conduct electricity, but these generalizations are still useful and whenever a new element is introduced it should be classified as a metal or non-metal if at all possible.

Most metals when heated in oxygen combine with the oxygen forming oxides. Usually these oxides do not dissolve in water but those of potassium, sodium, and calcium do dissolve. The liquid formed turns red litmus blue — this means that it is *alkaline*. This property leads to potassium, sodium and calcium being put together as a special family of metals.

The non-metals can also be divided into other families, of which one will be mentioned here. The elements fluorine, chlorine, bromine and iodine are members of the *halogen* family. The word 'halogen' means 'salt-former', and the second of these four members of the family reacts with sodium to form sodium chloride known commonly as salt. Common salt though is just one example of a wide range of substances all known as salts, the simplest examples being those formed between the halogens (salt-formers) and metals. The family resemblances are found mainly in their chemical reactions which will be studied later. Physically, chlorine is a yellowish green gas, bromine a reddish-brown liquid and iodine a black solid. It can also be noted here that all three of these elements are poisonous.

## 3. Compounds

Common salt has been mentioned as the product of the reaction between sodium and chlorine. This is a pure substance made by the combining together of two elements. In the combination the character of the separate elements is completely lost, a new substance being formed, so that the elements are said to be joined together chemically. *A pure substance containing two or more elements joined together chemically is known as a compound.*

The letters of the alphabet have to be put together in particular ways to make words and what words are to the letters, so compounds are to elements. It is the chemical combination of elements which gives rise to compounds. Compounds which have been mentioned in this chapter are lead nitrate which was seen to contain the elements lead, nitrogen and oxygen, mercury oxide containing mercury and oxygen, and several other oxides all of which contain oxygen.

The commonest substance of all is water which is a compound of the two gaseous elements, hydrogen and oxygen. Oxygen is in fact found in most common substances which is not really surprising since it is the most abundant element. Next in abundance is the element silicon and these two elements form sand, the chemical name of which is silicon dioxide. Another common dioxide is carbon dioxide which is mainly used to put the 'fizz' into mineral waters. A pure substance sometimes used in the kitchen is baking soda, for which the chemical name is sodium hydrogencarbonate which tells the chemist that the elements sodium, hydrogen, carbon and oxygen are present. Mention of the kitchen leads on to the unfortunate fact that some people after eating suffer from indigestion and the advertisements recommend 'milk of magnesia' as a cure. The pure chemical substance in milk of magnesia is magnesium hydroxide, a compound containing magnesium, hydrogen and oxygen. Acidity is often mentioned in the same advertisement as a cause of indigestion, and there is usually an acid to be found in the kitchen. This is acetic acid in vinegar and it is responsible for the taste

of vinegar. Acetic acid contains carbon, hydrogen and oxygen and it is now being given a new name — ethanoic acid. Another compound containing carbon, hydrogen and oxygen is glucose and yet another is sucrose (ordinary sugar). In fact the list of compounds containing only carbon, hydrogen and oxygen could be extended almost indefinitely. This used to be very puzzling to the chemist, but he did note that all these compounds came in the first place from plants or animals, that is from living organisms, and so these compounds were called *organic* compounds. The compounds obtained from air, land or sea were known as *inorganic* compounds. All organic compounds contain carbon and, usually, hydrogen. Oxygen is also very common in organic compounds and a few other elements such as nitrogen, sulphur and phosphorus are also sometimes found. Organic and inorganic compounds form the two main families amongst compounds, and there are some general features distinguishing the two families. Inorganic compounds usually have high melting points, organic compounds have low melting points or they are liquids. If inorganic compounds dissolve in anything it is usually in water, while organic compounds dissolve in other organic compounds. Inorganic compounds are hard and organic compounds soft. There are so many organic compounds and they are so important to life, that their study is a separate branch of chemistry known as organic chemistry.

It has been possible to show that some pure substances, whether elements or compounds are part of daily experience, but in general, the substances which we come across in everyday life are mixtures of elements, or mixtures of compounds, or mixtures of both. In the next three chapters air, land and sea will be investigated in order to find out how they are made up.

## Questions

1  What element is present when a glowing splint is re-lit by a gas?

2  Summarize the steps by which the elements present in lead nitrate could be obtained.

3  Read the text carefully and write down an acceptable definition of an element.

4  What are the main properties of metals and of non-metals?

In questions 5–8 select the one correct answer.

5  Which of the following statements is untrue?
   a Elements may be divided into two groups; these are metals and non-metals.
   b Lead and aluminium are metals.
   c Iodine, carbon and sulphur are non-metals.
   d Elements are only found in a chemical laboratory.
   e Lead bromide consists of two elements one of which is metallic and one non-metallic.

**6** A substance which is not decomposed by heat or electricity into other pure substances

    a has yet to be discovered

    b cannot be analysed

    c is called an element

    d is always a non-metal

    e is always metallic.

**7** Which of the following statements is *not* true?

    a Gold is an element.

    b Water consists of hydrogen and oxygen chemically combined.

    c Sodium is not shiny until cut therefore it is non-metallic.

    d Copper and iodine are elements.

    e Chlorine and carbon are non-metals.

**8** Which of the following statements is true?:

    a Salt is an element.

    b When two or more elements combine chemically, a compound is formed.

    c Water is a mixture of the elements hydrogen and oxygen.

    d Elements may be prepared by synthesis i.e. by the putting together of other substances.

    e The element potassium is found in baking soda.

**9** How would you distinguish between an element and a compound?

**10** What are the main differences between inorganic and organic compounds?

**11** With the help of reference books in your library, find out about the discovery of elements in the nineteenth century.

**12** Find out the names of the thirteen man-made elements — these are called the 'transuranic' elements, that is the 'beyond uranium' elements.

# 4
# Air

EVERYONE is so accustomed to having air all around, that its presence is often forgotten. Reference is made to empty cups, empty containers, empty rooms, when, in fact, they are full of air. Experiments show that air is really there; that it occupies space and has weight, so that air is a form of matter. The normal state of air is the gaseous state and its presence is so often forgotten because it is an invisible gas.

## 1. Pure substance or mixture?

Following on from the last chapter, in which pure substances were considered to be either elements or compounds, the question is 'Is air a pure substance, an element or compound, or is it a mixture?' From the time of Aristotle (384-322 B.C.) until nearly the end of the eighteenth century air was considered to be one of only four material elements, the other three being fire, earth and water. That this idea persisted for so long was probably due to the difficulty in handling gases. It was the work of Van Helmont at the beginning of the seventeenth century which started chemists thinking about gases. Among his many experiments, one is particularly relevant to this chapter.



Fig. 4.1 Van Helmont's Experiment on Burning

## EXPERIMENT 4.1

1. Use any convenient apparatus — Van Helmont floated the candle on a piece of wood and placed a large glass over it, (see Fig. 4.1).
2. Light the candle. When it is burning well, place the glass over it. What happens? Look especially at the level of water inside the glass.

Van Helmont saw the water rise and the flame go out, and explained the rise of the water level as being caused by consumption of part of the air. Why should only part of the air be used up? This question will be answered through experiments described during this chapter.

Robert Boyle, of whom mention has already been made, showed in 1673 that in the absence of air no burning took place. Potassium nitrate seemed to act in the same way as air, because Boyle showed that gunpowder (made of sulphur, carbon and potassium nitrate) would burn in a vacuum. Following Boyle, Hooke realized that when burning took place, the thing which burnt became associated with air in some way. He also considered that air and potassium nitrate had something in common. Mayow went still further showing clearly that in burning only part of the air is used up
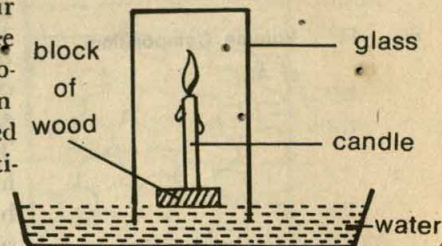
19

and this part is common to both air and potassium nitrate. Mayow also showed that things would not burn in that part of the air which was left over.

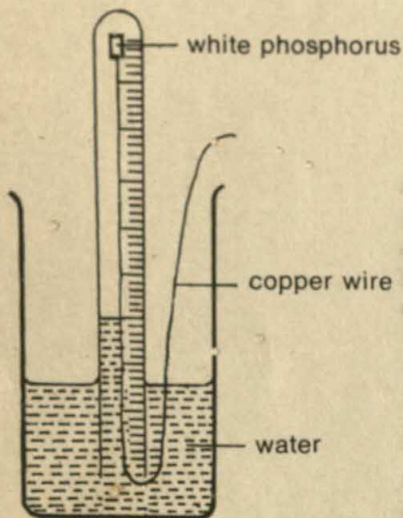In order to find out how much air is actually used up during burning, Experiment 4.2 can be carried out.

## EXPERIMENT 4.2

1. Make a loop at the end of a long piece of thick copper wire. Use this loop to support a piece of white phosphorus, so that it can be pushed to the end of a graduated tube as shown in Fig. 4.2. (A burette could be used).

2. Make the water level the same inside and outside, and measure the volume of air trapped over water.

3. The experiment takes a few days to complete. At the end of the experiment, make the water levels the same again and measure the volume of the remaining gas. (The accuracy of this experiment will be increased if the temperature and pressure are noted at the beginning and end of the experiment and then a correction can be made to allow for any change in these during the experiment.) This experiment shows that about 20% by volume of the air is used up in burning.



Fig. 4.2  Volume Composition of Air

(labels: white phosphorus, copper wire, water)

## 2. Phlogiston Theory

Although these facts were established before the end of seventeenth century, their true explanation was delayed for another hundred years. The explanation which was then accepted is known as the *Phlogiston Theory*. This stated that when a substance burnt, it lost 'phlogiston', the 'spirit of fire'. The candle placed under a jar goes out because the air in the flask becomes so full of phlogiston that it cannot hold any more, so the burning substance cannot lose any more and so cannot burn. The theory explained a certain number of facts and further experiments were carried out with results predicted by the theory, as should be the case with a good theory. However, some experiments, in which accurate weighings were performed, were inexplicable unless phlogiston were supposed to have negative weight.
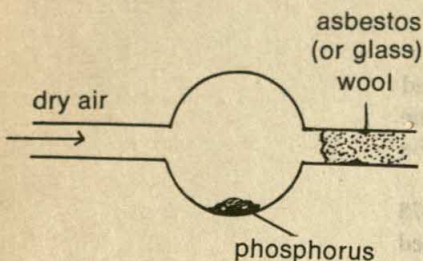


Fig. 4.3  Finding the Gain in Weight when Phosphorus burns

(labels: dry air, asbestos (or glass) wool, phosphorus)

## EXPERIMENT 4.3

1. Set up the apparatus shown in Fig. 4.3.
2. Put a small piece of dry white phosphorus in the bulb and weigh the whole apparatus.
3. Clamp it in a horizontal position and slowly pass air through it.
4. Gently warm the bulb to ignite the phosphorus and let it burn for several minutes.
5. Allow the apparatus to cool and weigh it again.

## EXPERIMENT 4.4

1. Half fill a crucible with magnesium dust (or turnings). Put its cover on and weigh it.

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2. Heat the crucible as shown in Fig. 4.4. Lift the lid with tongs at regular intervals, taking care to prevent smoke escaping.

3. When the magnesium no longer burns, allow the crucible to cool and weigh it again.



Fig. 4.4 Finding the Gain in Weight when Magnesium burns

Experiments 4.3 and 4.4 both show that there is an increase in weight when a substance burns. To contradict these results, the results of burning a candle can be quoted from Experiment 4.5.

### EXPERIMENT 4.5

1. Place a candle on a watch glass and weigh it.

2. Light the candle and allow it to burn for a few minutes, taking care not to lose any of the melted wax.

3. Blow out the candle and re-weigh it.

In this experiment a loss of mass is found, and the burning of coal or wood or other fuel would apparently give the same result accounted for by the loss of phlogiston. But it should be remembered that in Experiments 4.3 and 4.4, care was taken to catch smoke produced during the burning, while no such precaution was taken in Experiment 4.5.

Making use of knowledge which will be explained later, it is possible to set up a piece of apparatus to trap the products in the smoke of a burning candle (see Fig. 4.5). Calcium chloride traps water vapour and soda-lime traps carbon dioxide. If the apparatus is suspended from the arm of a balance and weighed, it will be found that after the candle has burnt for a while there will be an increase in weight.

So, burning results in an increase in weight, and the phlogiston theory cannot explain this satisfactorily. This means that another explanation must be sought. Reviewing information so far obtained, it is known that air is required for burning, part of it is used up in burning, the part which remains does not allow things to burn, and there is an increase in weight when a substance is burned.

From these results it would appear that air is made up of at least two parts, so that it cannot be considered as an element. It might also seem reasonable to consider that the part of the air which is used up in burning is added to the burning substance accounting for the increase in weight. Can this be demonstrated?

Going back in time, attention can now be focussed on the end of the eighteenth century. A Swedish chemist named Scheele discovered in 1772 a gas in which substances burned better than in air, and which relighted a glowing splint. He called this gas 'fire air' and identified it with the gas in the air which was used up in burning — the other gas he called 'foul air'. When 'fire air' and 'foul air' were mixed to give 20% 'fire air' and 80% 'foul air', the mixture had all the properties of ordinary air. In England, two years later, Priestley made similar discoveries; Experiment 4.6 is like those carried out by Scheele and Priestley.
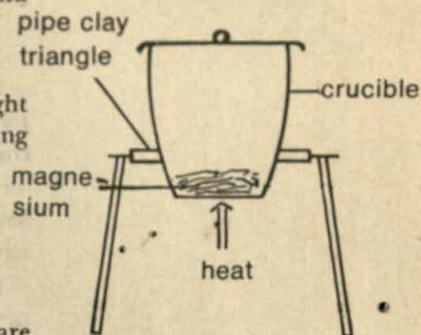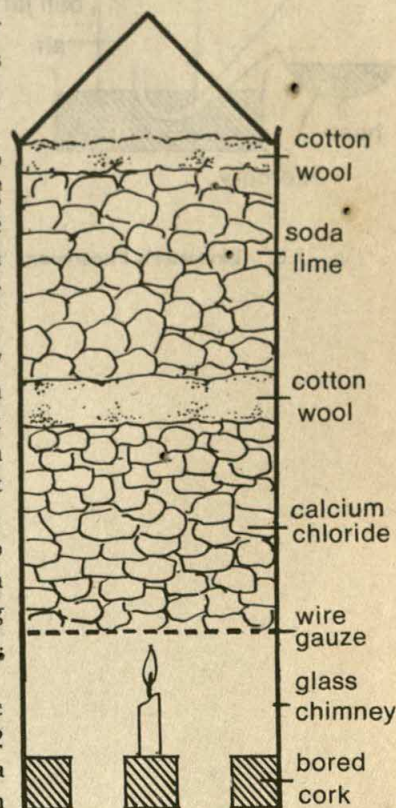


Fig. 4.5 Finding the Gain in Weight when a Candle burns

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## EXPERIMENT 4.6

1. Put a little mercury oxide in a test tube and heat strongly.
2. Put a glowing splint into the test tube. What happens?

A substance must be coming out of the tube to make the glowing splint relight. Since it cannot be seen, it must be an invisible gas. Priestley was convinced that the phlogiston theory was correct and so he called this gas 'dephlogisticated air'. Priestley told a French chemist Lavoisier of his discoveries and this enabled Lavoisier to replace the phlogiston theory with a new one, which today is accepted as fact.

By 1778, Lavoisier had reached the conclusion that 'the whole of the air in the atmosphere is not in the respirable state; it is the respirable part which combines with metals during their burning and what remains is incapable of sustaining the respiration of animals or the burning of substances'. Lavoisier confirmed his view of the composition of the atmosphere by the famous experiment described in the next paragraph.
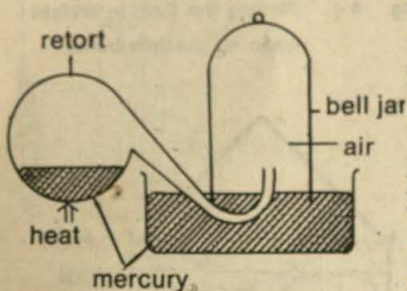
### 3. Lavoisier's experiment



Fig. 4.6    Lavoisier's Experiment

Lavoisier heated 4 oz. of mercury using the apparatus shown in Fig. 4.6. The volume of air in the bell jar and retort was 50 in³. After a time he noticed the formation of red specks and scales on the surface of the mercury. After twelve days (!) there was no increase of scales; the heat was removed, and the experiment stopped. The air had contracted to 42 in³, and the gas left was given the name *azote* by Lavoisier. The scales were collected and found to weigh 45 grains. They were put into a small retort and 8 in³ of a gas, 'much more capable of supporting respiration and combustion than ordinary air', were obtained, together with $41\frac{1}{2}$ grains of mercury. When this gas was added to azote, ordinary air was formed. (In the light of modern knowledge these results are extremely accurate). In this experiment, Lavoisier showed that part of the air is used up in burning. The part which is used up has combined with the mercury, this being shown by the recovery of the exact amount of lost air on heating the scales. Lavoisier called the gas used up in burning, 'oxygen' and azote was given the name 'nitrogen'. The mixing of these two gases in roughly the right quantities gives ordinary air. The exact quantities are not fixed so air is a mixture and, as will be shown later, it contains more than the two elements oxygen and nitrogen.

### 4. Combustion and oxidation

A study of burning has shown air to be a mixture, and a description of burning has also emerged. Burning (or *combustion*) is the combination of a substance with the oxygen of the air, resulting in the formation of new substances. The substances formed by burning are called oxides and the formation of oxides by adding oxygen is an example of *oxidation*. So, burning is an oxidation process and the term is usually limited to oxidation reactions in which heat and light energy are produced at the same time.

## 4. Respiration

Mayow, Scheele, Priestley and Lavoisier were all aware of the great similarity between combustion and *respiration*. Respiration is the way in which animals and plants provide themselves with energy for the activities of life. Higher animals such as man provide themselves with the oxygen required for respiration by breathing. Without oxygen, life as it exists on Earth would be impossible. The place of oxygen in respiration was first suggested by the experiments of Mayow. Just as a candle placed under a glass uses up some of the air and then goes out, so placing a mouse under a glass leads eventually to the mouse ceasing to breathe when about the same amount of air had been used up. Scheele also found that a rat and flies died in confined volumes of air. After Priestley had discovered oxygen, he showed that a mouse lived longer when confined in it than in ordinary air. Finally, Lavoisier said 'respiration is a combustion, truly very slow but otherwise perfectly similar to that of charcoal'. Charcoal is taken as the example here because it can be shown that air breathed out contains more carbon dioxide than that breathed in, and carbon dioxide is the product of burning charcoal. The slow process of respiration is made up of many steps, which can be summarized as follows:

$$\text{Food} + \text{oxygen} \longrightarrow \textit{Energy} + \text{water} + \text{carbon dioxide}.$$
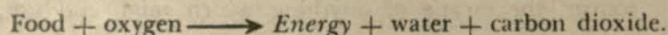
## 5. Photosynthesis

It is not only respiration that gives up carbon dioxide to the air, the burning of most fuels — wood, coal, charcoal, oil — gives carbon dioxide as one of the products. This means that carbon dioxide is another gas in the mixture known as air. It also raises a problem — all burning processes use up oxygen and many put carbon dioxide into the atmosphere, so why is it that the amounts of oxygen and of carbon dioxide in air are nearly always constant? The answer to this question gives added significance to the part played by plants in keeping life going on Earth. As plants prepare their food in their green leaves they take in carbon dioxide and release oxygen. For this process to take place, light is required and it is a process in which complex substances are built up from simpler ones, so it is known as *photosynthesis*. Photosynthesis is discussed in more detail in the Biology course; here it is important as the means by which the accumulation of carbon dioxide in the air is prevented.

## 6. Noble gases

Density as a means of determining purity has already been mentioned and it was a difference in density measurements which led to the discovery of five more gases in air. In 1892 Lord Rayleigh found that nitrogen obtained from air by removing the oxygen was denser than nitrogen extracted from other chemicals. After two years of work it was found that the greater density of atmospheric nitrogen was due to the presence of an unreactive gas, which was given the name argon. In the next ten years, five similar gases were discovered — helium, neon, krypton, xenon and radon. These gases were called *inert* gases because they could not be made to react with any other elements. Very recently, it has been found that they

can be made to react, under certain conditions, and they are now referred to as the *noble* gases.

## 7. Air pollution

The heat of the Sun is always causing water to evaporate so that air also contains water vapour. The amount is variable and may be as much as 4%. Any other substance found in air can be considered a pollutant — that is, waste material which offends the sense of others or is harmful to their well-being. Most offence is caused by fires used for cooking and heating. These fill the air with smoke, grit, ash and sulphur dioxide. If oil is used, even more sulphur dioxide is produced. The exhaust of cars sends out oxides of nitrogen, poisonous carbon monoxide, and poisonous lead compounds. Waste materials and sometimes the escape of wanted materials from factories may pollute the atmosphere — fluorine compounds from brickworks, cyanides from steelworks, oxides of sulphur and nitrogen from factories where sulphuric acid and nitric acid are made. After the Industrial Revolution many of these pollutants were allowed to pollute the atmosphere without any control or concern for their effects. Men are more conscious of their environment at the present time, and much more effort is made to control the escape of anything which might pollute the atmosphere.

A summary of the gases present in air is given in Fig. 4.7.



78% nitrogen

21% oxygen

1% other gases, including argon, carbon dioxide and water vapour
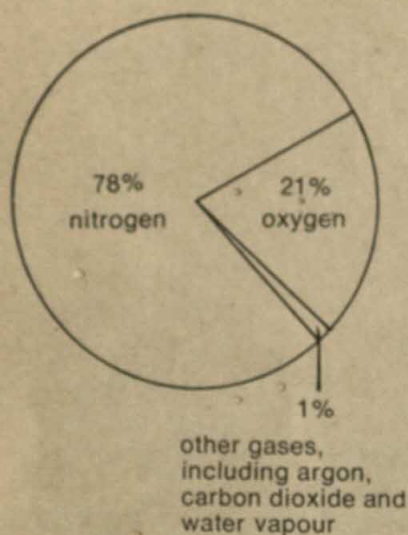
Fig. 4.7 Composition of the Air by volume

### Questions

1 In what state of matter are the elements in the air? Are they free or chemically combined with one another?

2 Since the air we breathe out contains carbon dioxide, why does the amount of carbon dioxide in the air not increase as time goes on?

3 If your room caught fire, why would you shut the door before getting help?

4 Explain why magnesium gains in weight but a piece of coal appears to lose weight when each is burnt in air.

5 What are the five main constituents of the air?

6 How many cubic metres of oxygen are there in 100 $m^3$ of air?

7 Name five noble gases found in air. Give one property that is common to them all.

8 How could you show the similarity between burning and respiration?

9 What impurities are likely to be present in the air?

10 Write notes on
   a The causes of atmospheric pollution.
   b The harm which polluted air causes to health.
   c The discovery of the noble gases.
   d The uses of the noble gases.

# 5
# The Sea

A VIEW of the surface of the Earth such as that in Fig. 5.1, shows just how much of the surface is covered with water. In fact, about seven-tenths of the surface is water. Approximately 98% of this water is in the oceans and most of the remainder is locked up as ice, particularly in the polar ice-caps of the Arctic and Antarctica. The vast amount of water required for life represents a minute fraction of the total amount available. Freshwater (water that is not salty) in rivers, lakes and groundwater is only 0.027% ($\frac{27}{100\,000}$) of the whole. As the freshwater is used up, it is replaced from an even smaller amount — the 0.000 053% which moves around in the atmosphere.



Fig. 5.1    Water on the Surface of the Earth

Pure water does not occur naturally. The water vapour in clouds is fairly pure, but as it falls to the ground as rain, carbon dioxide and oxygen are dissolved in it. Near the sea, it may also dissolve salts from sea spray. In industrial areas it may dissolve some dust and the oxides of sulphur and nitrogen. If the rain falls on porous rock it soaks through and collects beneath the surface of the Earth as ground-water, and this ground-water will contain various dissolved substances depending on the nature of the rocks through which it has passed. In other places, water runs off the surface forming streams and rivers. As the rivers flow towards the sea, the water dissolves other substances and becomes more and more impure and polluted. In some areas impurities and pollution are increased by industrial waste and sewage. The sea receives all these impurities, so that dissolved materials represent 3.6% of the whole.

## 1. Solvent and Solute

The sea is full of so much dissolved matter, because water dissolves very many substances. In fact, all the naturally occurring elements dissolve, or form compounds which dissolve, so that they are all present to some degree in the sea. Because water dissolves so many things it is often referred to as the universal *solvent*.

The word 'solvent' may be new to you, and it is necessary to consider its meaning together with the meanings of several other words which are part of the vocabulary of the chemist when he talks about one substance dissolving in another.

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## EXPERIMENT 5.1

1. Half fill a test tube with water and add a little powdered copper sulphate. Shake the test tube vigorously. What happens?
2. Repeat the experiment with salt and sugar instead of copper sulphate.

In Experiment 5.1, the solid particles disappear and a clear liquid is left. The copper sulphate, salt and sugar have dissolved in the water and the resulting liquid is called a *solution* — a solution of copper sulphate, or salt, or sugar in water. Because these solids dissolve in water, they are said to be *soluble* in water. Substances which do not dissolve are *insoluble*. Experiment 5.2 divides substances into those soluble in water, and those which are insoluble.
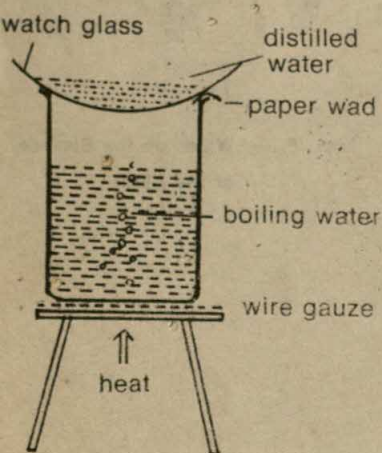
## EXPERIMENT 5.2

1. Take some distilled water in a watch glass and place it over a beaker of boiling water as shown in Fig. 5.2. When all the water has evaporated, hold the watch glass up to the light. Is there anything left behind? (This is a control experiment, showing that the water which is going to be used for the next stage, does not itself contain any dissolved solids).
2. Put small equal volumes (e.g. so as to fill the rounded part of a test tube) of potassium nitrate, manganese dioxide, calcium chloride, potassium permanganate and sulphur into five test tubes. Add distilled water to each tube to a depth of about four centimetres. Shake each tube vigorously and then filter, collecting the filtrate on a watch glass. Evaporate the water and see if there is any residue. Which solids are soluble and which are insoluble? How do you know?



watch glass
distilled water
paper wad
boiling water
wire gauze
heat

Fig. 5.2 **Investigating the presence of dissolved solids in water**

A substance insoluble in one liquid may be soluble in another. For example, sulphur is insoluble in water, but it dissolves in both carbon disulphide and xylene. A liquid which will dissolve something is called a *solvent*. Water is a solvent for copper sulphate, sugar, salt, potassium nitrate, calcium chloride, potassium permanganate and countless other substances. Carbon disulphide is a solvent for sulphur and phosphorus. The substance which dissolves is called the *solute*. Solvents other than water are often used to remove stains caused by tar, oil, grease or paints from clothes. In 'dry cleaning' the clothes are treated with a liquid which is a solvent for grease and dirt. The process is described as dry because the liquid is not water.

The solutes discussed so far have been solids, although at the beginning of the chapter mention was made of gases in the air dissolving in rain water. The fact that gases dissolve in water has important consequences, perhaps the most important being the existence of life in water because oxygen dissolves in water. Coca-Cola and all similar drinks are fizzy because of the carbon dioxide dissolved in them; pressure is applied to make more carbon dioxide than usual dissolve. Water is a major element in the

wearing away of rocks — the process of erosion, and the gases dissolved in water can speed up this process. For example, water containing dissolved carbon dioxide will react with limestone and related rocks producing a soluble substance. Acetylene, a gas used with oxygen in welding, is stored by dissolving it under pressure in acetone. Liquids can also be solutes, if they dissolve in other liquids. Beer, wines and spirits all contain alcohol dissolved in water. In the motor-scooter, oil is dissolved in the petrol used in the engine.

## 2. Solution

If a substance is insoluble then it can be removed from the solvent by filtration. The particles of a soluble substance pass through a filter. If an insoluble substance is shaken up with water, the particles spread throughout the water, but on standing they settle again to the bottom of the test tube. A solution, whether it is observed at the top, the bottom, in the middle or anywhere else, is always the same, that is to say, a solution is homogeneous. *A solution is a homogeneous mixture of two or more substances.*

Solute + solvent ⟶ solution.
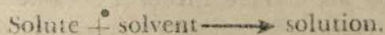
## EXPERIMENT 5.3

1. Take a boiling tube and put some ammonium chloride in it to a depth of about 2 cm. Add cold water until its depth is 3 cm. measured from the bottom of the tube. Shake the mixture hard for a few minutes. Does any of the ammonium chloride dissolve? Does it all dissolve?

2. Now warm the tube and shake again. Does any more ammonium chloride dissolve?

3. Finally, boil the mixture, and see what happens to the ammonium chloride.

## 3. Saturated solution

Experiment 5.3 shows two things. First, the cold water would not dissolve all the ammonium chloride. When it had dissolved all that it could, the solution was *saturated*. Secondly, as the temperature increased more solid dissolved, until a sufficiently high temperature was reached for it all to dissolve. In this final state, the solution may or may not be saturated and the only way to find out is to add more solid. If this does not dissolve the solution is saturated; if it dissolves then the solution is *unsaturated*. Putting this information together, the meaning of 'saturated' can be expressed as follows:

*A saturated solution is one which, in the presence of excess solute, will dissolve no more solute at that particular temperature.*

## 4. Solubility

At a particular temperature the amount of solid which will dissolve depends on the amount of solvent used and on the nature of the solute.

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To make comparisons between one solute and another the amount of solvent should be the same. For example, about six times as much sugar as salt will dissolve in 100 g of water at 20°C. The amount of a solute which will dissolve in 100 g of water is known as its *solubility*.

*The solubility of a solute is the number of grams of the solute in a saturated solution containing 100 g of solvent at a particular temperature.*

Generally, the solubility of a solid increases with rising temperature. Sometimes there is not much increase — the solubility of salt is 35.2 g per 100 g of water at 0°C and 39.2 g per 100°C of water at 100°C. Sometimes there is a marked difference — with potassium nitrate the corresponding figures are 13.5 g and 245 g. Gases are more soluble in cold liquids than in hot. For example, 0.28 g of carbon dioxide will dissolve in 100 g of water at 5°C, but less than half as much at 25°C.

## 5. Compounds in sea water

In this chapter, solutions were introduced by considering the sea. The sea contains many solutes because of the unique properties of water as a solvent. Some of these are extracted from the sea because it is worthwhile doing so. In other cases, any extraction process is too expensive. For example, in a cubic kilometre of sea-water, there may be gold worth about Rupees 2 crore, but the cost of extraction at present would be about Rupees 10 crore. Fig. 5.3 shows the main constituents of sea water in terms of the separate elements.



others 0.5%
sodium 1.1%
chlorine 1.9%
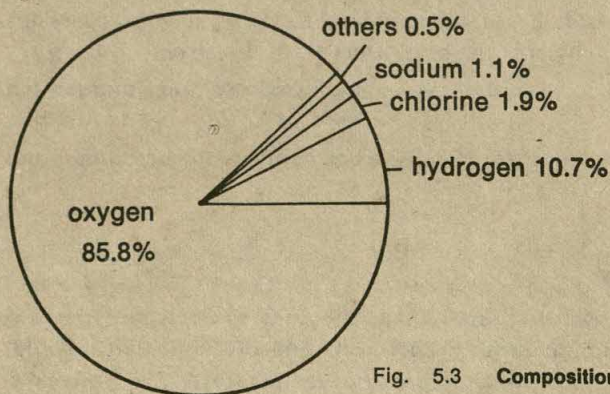hydrogen 10.7%
oxygen 85.8%

Fig. 5.3    **Composition of the Sea by Mass**

The table below is a list of the main compounds found in sea water.

| Compound | Parts per 1000 (approx.) |
|---|---|
| Sodium chloride | 27.2 |
| Magnesium chloride | 3.8 |
| Magnesium sulphate | 1.7 |
| Calcium sulphate | 1.3 |
| Potassium chloride | 0.9 |
| Calcium carbonate | 0.1 |
| Magnesium bromide | 0.08 |

In this list, those which are profitable to extract at present are sodium chloride, magnesium chloride, potassium chloride and magnesium bromide. Only a small part of the sodium chloride so obtained is used in food and for preserving food. Many other substances are manufactured from salt, for example, sodium and chlorine, sodium hydroxide and sodium carbonate. Large quantities are also used in the manufacture of pottery, in dyeing and in curing leather. Details of the uses to which sodium chloride is put will be given at a later stage in this course. Magnesium chloride and potassium chloride are sources of the metals magnesium and potassium. Magnesium bromide is used to make bromine.

## 6. Pollution of sea water

Until very recently the sea was used as a rubbish dump, without any regard for the consequences. Dumping still goes on, but more attention is now paid to the problems of pollution. In Chapter 4, pollution was explained as occurring if when a material is thrown away, it offends other people or is harmful to them. It is offensive to walk along a beach covered with oil washed out of the holds of an oil tanker. It has been suggested that in a generation from now a stroll along a beach will be impossible, since the beach will have become a *cesspool*. In Japan, careless disposal of mercury wastes into the sea resulted in mercury accumulating in fish and since the Japanese people love to eat fish, they fell victims to mercury poisoning. The name of the place, Minamata, is now associated with the disease. Minamata disease caused at least 71 deaths and paralysed about six hundred people. In India, Maharashtra State has pioneered a proposal on Environmental Control and it must be remembered that the sea is part of the total environment in which we live. Our Central government is considering a Bill to set up a Pollution Board at the all-India level, and this is a step forward which few other countries have as yet taken. One of the aims of this book is to present the hazards of pollution and then later to discuss ways of preventing pollution.

## Questions

1 What is the difference between *dissolve* and *melt?*

2. When copper sulphate is dissolved in water, it gives a *clear liquid*. When this liquid is left in an open dish, *the liquid which has dissolved the solid* evaporates and the *dissolved solid* is left as blue crystals.
   Replace each group of words in italics with *one* suitable word (not the name of a particular substance)

3 What is a 'saturated solution'?

4 What is meant by 'solubility'?

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5 How would you show simply whether a given solution is
(*a*) unsaturated, (*b*) saturated.

6 What are the factors which affect the solubility of solids?

7 A colourless liquid X is either pure water, or water containing some dissolved solid. How would you find out which it is?

8 How could you show that tincture of iodine is a solution?

9 Is 'dry cleaning' a dry process? How is it done?

10 Give as many examples as you can of the use of solvents and solutions in everyday life and industry.

11 Write notes on:

a The pollution of sea-water.
b Dissolved solids in sea-water and their uses.

# 6
# The Land

In the past, the sea was used to some extent as a source of sodium chloride for food and food preservation, and the air was not used for anything, although of course, it has always been necessary for life. However, the civilizations of the past were built on the great wealth to be found on and within the land, and it is the purpose of this chapter to show the extent to which the land is a source of the elements and compounds which today are regarded as essential.

## 1. Gold, Copper and Silver: extraction and use

The form in which a substance occurs in the Earth's crust and the ease with which it can be extracted has had important consequences. This can be shown by tracing the history of the use of metals. Gold is not very abundant, being included with 77 elements making up less than 0.1% of the Earth's crust, or put another way, 100 000 kg of gold-bearing rock may only contain 1 kg of gold – and that is the best concentration! Despite this, gold was probably the earliest metal to be used by man because it occurs in the *native* metallic form, that is as the element itself. Gold ornaments have been found dating back to the Neolithic age – 6,000 B.C. onwards. The next metal known was probably copper and some think it was known before gold in Egypt. Copper does occur 'native', Kerala being one of the places where it is found in the native state. It seems, though, that the Egyptians obtained it from an ore known as malachite. This is basically copper carbonate and Experiment 6.1. shows how copper can be extracted from this using charcoal.

## EXPERIMENT 6.1

Put some copper carbonate in a hollow in a charcoal block. Using a blow-pipe as shown in Fig. 3.1, heat the carbonate and block. A brownish powder will be obtained, which is copper. However this may go black, because at the temperature of this reaction air may add to the copper giving black copper oxide.

The Egyptians probably got their copper by heating the ore malachite in charcoal fires. Copper objects have been found dating back to 3500 B.C.

Gold, silver and copper were known to the Sumerians of Mesopotamia at least as early as 3400 B.C. Silver, like gold, can occur native or in ores

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which are easily converted to silver. Again this accounts for its early usage, despite the fact that its occurrence throughout the Earth's crust is only to the extent of about 0.1 g in every 1 000 000 kg of rock. Dating from about 3000 B.C., specimens of bronze have been found at the site of Ur of the Chaldees; bronze is a mixture of the metals copper and tin. Such a mixture is known as an *alloy*. The period from 3000 B.C. onwards is known as the bronze age. Tin is not found in many places and the source of tin for this early bronze is not known. In some specimens of bronze, lead is found instead of tin and sometimes antimony. The amounts of all these elements in the Earth's crust are extremely small; their discovery, as has already been mentioned, was dependent upon them occurring native or in compounds from which they could be easily extracted. The basic chemistry of the early processes of extraction, could be summarised as:

$$\text{Metal compound} \xrightarrow{\text{heat}} \text{metal oxide.}$$

$$\text{Metal oxide} + \text{charcoal} \xrightarrow{\text{heat}} \text{metal} + \text{carbon dioxide.}$$
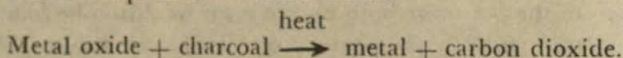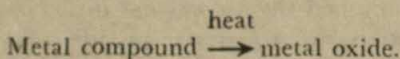
The addition of oxygen has already been called oxidation. The removal of oxygen is an example of the process known as *reduction*. There may be a number of stages by which a metal is obtained from the rocks of the Earth's crust but the last one is always reduction. Reduction is carried out by a reducing agent, wood charcoal being used in this capacity from earliest times. It is still used in Sweden but, elsewhere, it has been mostly replaced by coke which is obtained when coal is heated in the absence of air. Charcoal and coke are forms of the non-metal carbon although they are not 100% pure.

## 2. Iron

The fourth most abundant element in the Earth's crust is iron, (see Fig. 6.1) but it was not until 1500 B.C. that it came into general use and that the Iron Age can be said to have started. What does this tell you about the compounds of iron, in relation to those of copper, lead and tin? Iron was known before this time, because meteorites sometimes consist of as much as 97% native iron, but this can hardly be considered as coming from the Earth's crust.

An alloy still in use today is brass containing copper and zinc. Brass dating back to about 1200 B.C. was found in Palestine, so zinc has been known since that time even though it is only present in the Earth's crust in small quantities. Indian coins containing copper and nickel date from 235 B.C., so nickel must have been known from at least that date.

## 3. Non-metallic elements

Summarizing knowledge of the pre-Christian era, as far as metals are concerned, the land had provided man with gold, silver, copper, tin, lead, antimony, iron, zinc and nickel. What of the non-metals? Carbon in the form of charcoal was a necessary item in the extraction of metals. Sulphur has also been known from ancient times being found native in the craters of extinct volcanoes and also in large quantities on the island of Sicily.

Apart from these two non-metals, no other non-metallic element was known until the discovery of phosphorus in 1669. The element mercury is a liquid metal, but although it was mentioned by Aristotle in 350 B.C. it was only admitted to be a true metal after 1759 when it was frozen to a *malleable* solid.
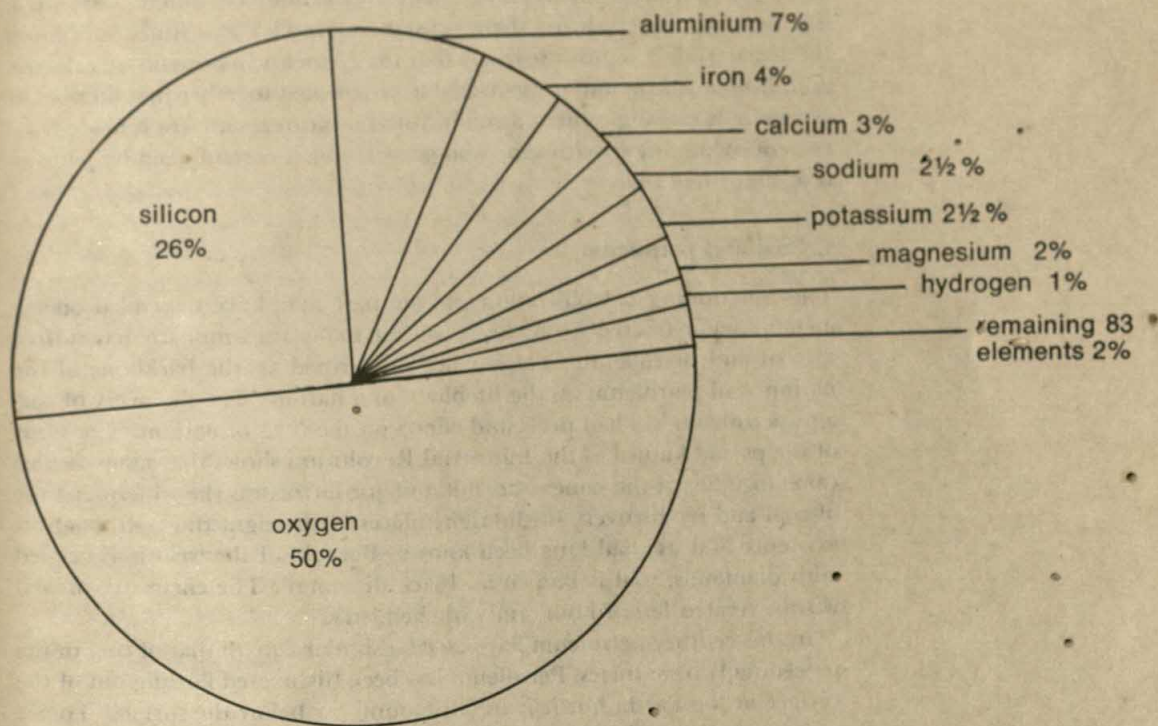
aluminium 7%

iron 4%

calcium 3%

sodium 2½%

potassium 2½%

magnesium 2%

hydrogen 1%

remaining 83 elements 2%

silicon 26%

oxygen 50%

Fig. 6.1 Proportion by weight of Elements in the Earth's Crust

## 4. Compounds—clay and glass

The Earth's crust is not only to be regarded as a source of elements, although it was the extraction and use of the various metallic elements which characterized earlier civilizations. The more abundant elements (see Fig. 6.1) silicon, aluminium, calcium, sodium, potassium and magnesium all form compounds which are important, and in some cases possibly more useful than the elements themselves. For centuries men have known how to make bricks, tiles, and earthenware vessels from clay. Clay is a complex of silicon, aluminium, oxygen and hydrogen. The ancient art of working clay has become a modern science and industry — the ceramic industry. Ceramics are found in nuclear power plants and in the engines of rockets. A more down to earth use is in the porcelain insulators on the poles carrying overhead electric cables. Another art turned to science is that of glass making. The manufacture of glass on a large scale apparently began in Egypt about 1370 B.C. The main constituent of glass is sand which is a compound of silicon and oxygen. Mixed with the sand are various metal compounds. In the Egyptian glass, sodium carbonate was used.

This was found in lakes near Alexandria. Window glass is made by melting sand with sodium carbonate and calcium carbonate which is the chemical substance of which rocks like limestone, marble and chalk are composed.

Buildings are built using bricks from clay, sandstone, limestone, marble, and other rock materials depending on what is available locally. In modern buildings and other structures cement and reinforced concrete are used. The starting materials for these substances are clay and limestone. From these materials it is possible to say that the elements in cement are calcium, aluminium, silicon and oxygen. These are formed together in a number of compounds making cement a complicated mixture. Concrete is made from cement by mixing it with sand and gravel, and it is reinforced by pouring it around steel rods.

### 5. Coal and petroleum

The functioning of civilizations in the past may have depended on the metals they extracted from the land, but today the emphasis has shifted to coal and petroleum. Coal has been described as 'the backbone of the nation' and petroleum as 'the lifeblood of a nation'. The discovery of coal and petroleum has had profound effects on the lives of nations. The study of the period known as the Industrial Revolution shows that many factors came together at the same time, but a major factor was the widespread use of coal and its discovery in the right places at the right time, although its existence and use had long been known. Because of the wealth associated with diamonds, coal is known as 'black diamond'. The chemistry of coal will be treated later in our study of chemistry.

In this century petroleum has played a similar role to that of coal in the preceding two centuries. Petroleum has been discovered flowing out of the surface of the Earth, but it is usually found far below the surface. To get at it, oil wells are drilled and this was first done in 1859. Petroleum when it was first discovered had only limited use until the invention of the internal combustion engine (1883) and its use in the motor car (1885). About half of the petroleum produced is required for petrol and one quarter for lubricating oils. The remainder is used for a wide variety of products which would be too long to list at this stage. Many of the substances once obtained from coal, are now obtained from petroleum. In keeping with its economic importance, petroleum has been described as 'liquid gold'. This subject is dealt with more fully at a later stage.

### 6. Aluminium

This chapter concludes with a mention of the third most abundant element in the Earth's crust — aluminium. Despite its abundance, it was not until 1808 that Davy isolated it from its compounds. Davy's aluminium was impure and Oersted obtained a purer form of the metal in 1825. On account of the difficulties of its extraction, another sixty years passed before any use could be made of the metal. During this period it was very expensive, costing between six and seven thousand rupees per kilogram. Two men in 1886 discovered a process in which electricity was used to split up an aluminium compound. One man, Hall, worked in America and the

other, Heroult, worked in France. Details of their processes differ, but the main ideas are the same. Pure aluminium oxide is obtained from an ore called bauxite which contains 55% aluminium oxide. The pure oxide is dissolved in another aluminium containing compound, cryolite, found in Greenland. When electricity is passed through this solution, aluminium is obtained. The only drawback of this method is that it requires large quantities of electricity, but even so it is possible to buy utensils of aluminium for about Rs 15 per kg.

In this chapter, a beginning has been made with the study of the chemistry of the Earth's crust. This crust is a mixture of elements and compounds, and extracting the pure substances from this mixture is a major operation. The land is still the main store-house of the Earth and investigating this storehouse reveals the wealth of the Earth's crust. Many of the substances mentioned in this chapter will be studied in greater depth later and more details of their chemistry will be given. This will lead to an even greater appreciation of the role of the chemist in modern society.

## Questions

1  Which elements occur 'native' in the Earth's crust?
   Find out the name of another element occurring 'native' in the Earth's crust which is not mentioned in this chapter.

2  Outline the chemistry of the extraction of a metal from its ore.

3  What is an alloy?

4  What are the metals in

   a bronze
   b brass?

5  What metals are contained in the following ores?
   a malachite
   b bauxite.

6  Give a simple meaning of the word 'reduction'.

7  The metals which were first discovered, occur in the Earth's crust in very small amounts. Why were they discovered so early on?

8  What is a meteorite? What metal was first obtained from meteorites?

9  What is unusual about the metal mercury?

10  Name some of the things that are made from aluminium.

11  From memory, write down a list of all the elements you can think of. Check the list with all those mentioned in Chapters 3, 4, 5 and 6.

# 7
# Our Total Environment

## 1. The Universe

IN its widest sense, our total environment is the Universe. The study of the Universe is the concern of the astronomer. The tools he uses such as the telescope and the radio-telescope operate according to well known physical principles. When an astronomer describes the movements of the planets and stars, he uses the laws of mechanics such as Newton's law of gravitation.

Another important discovery by Newton was to pass light through a glass prism and show that ordinary light was made up of a number of different colours. The pattern of colours is known as a *spectrum*. The fact that each element has its own special spectrum was mentioned in Chapter 3. The significance of this, in thinking about our total environment, is that the light from the Sun and stars can be examined in a similar way. This branch of Chemistry (or Physics?) is known as *spectroscopy* and was developed by Bunsen (who also invented the burner) and Kirchhoff (remembered also for laws relating to electricity). Writing about their work, Bunsen said, 'The way is pointed out by which the material composition of the Sun and fixed stars can be ascertained'. The material composition of the Universe has been shown to be the same as that of the Earth. Although the proportions may differ, the Sun, the stars and the planets are made up of the same elements with which we are familiar. The principal elements discovered on the Moon are, in order of decreasing abundance, oxygen, silicon, iron, magnesium, calcium, aluminium, and titanium. Compare this list with the seven most abundant elements in the Earth's crust (see Fig. 6.1).

In the last few years it has become clear from a study of stars in different parts of the Universe, that the making of elements is linked with processes going on in all stars. In the Sun energy is produced continually by a process in which hydrogen is changed into helium. This energy makes life possible on Earth (see later in this chapter). In other stars helium is being turned into carbon. Elsewhere other elements are being made. It also seems as if whole stars can explode, forming other elements, and scattering these through the Universe. So, chemistry merges with astronomy and the vastness of our total environment becomes seemingly more manageable.

To bring us down to Earth, consider meteorites which present further evidence of the oneness of the Universe. On a clear night shooting stars may be seen streaking across the sky. These shooting stars, called meteors by astronomers, are lumps of rock entering our atmosphere at high speed. Meteors which land are called meteorites. Meteorites as a source of iron

have already been mentioned; silicon, oxygen, graphite (sometimes small diamonds), sulphur, phosphorus, nickel and cobalt are also found in meteorites. Since meteorites come from space, it is possible to say that these elements are present in the Universe as they are on Earth.

## 2. Clouds, Winds and Rain

The chemist is very much concerned with getting pure substances and air, sea and land have all been considered as sources of these pure substances. Man has applied his knowledge to extracting pure substances, but there is an important process which has been going on since the Earth took shape as a planet with air, sea and land. This is the one in which energy from the Sun causes water to evaporate. As the water vapour rises it condenses and clouds are formed which deposit rain when they are further cooled. In physical terms, evaporation followed by condensation takes place. This is the same process used by the chemist in distillation, for example, to get pure water from sea water. So it is that the clouds contain distilled water, 98% coming from the oceans and seas.

The clouds do not stay still, but are moved along by the winds. The basic wind pattern is determined by the shape of the Earth, its tilt on its axis and its spin on this axis. Imposed on this pattern is the effect of the various land masses. As far as India is concerned, it is the land mass of India which is responsible for the annual monsoon. The northern land masses heat up more quickly than the vast ocean to the south. This causes the formation and development of an air current from the high pressure areas over the oceans towards the low pressure areas over the land. As these air masses blow over the large expanse of the Indian Ocean, they collect large quantities of water vapour, which is ultimately deposited as rain throughout India. The study of the weather is becoming an exact science known as meteorology. This science relies heavily on a knowledge of physics, and might also be referred to as a branch of physical geography. Geography is very much concerned with the environment. Much of the chemistry of the land discussed in the previous chapter would find a place in a study of geography. This indicates that traditional subject divisions are rather artificial.

## 3. Nitrogen and plant growth

Although water in clouds is distilled water, as it falls to Earth various other substances become dissolved in it. Some of these are useful and some might be harmful (the pollutants mentioned in Chapter 4). An example of an important dissolved substance is nitric acid in very dilute solution. Nitric acid results from dissolving nitrogen dioxide in water. Nitrogen dioxide is formed by lightning which provides sufficient energy for the oxygen and nitrogen of the atmosphere to combine together. The immediate product is called nitrogen monoxide (nitric oxide) but this immediately joins with more oxygen to form nitrogen dioxide. Nitric acid contains the element nitrogen essential for growth in plants and animals. Reacting with substances in the soil, the nitric acid produces soluble salts called nitrates. These are absorbed by the roots of plants and built into

the complex compounds found in living matter. Since it is only plants which can carry out this building up process, all animals, including Man, are dependent on plants. Here the field of biology is entered and in particular the study of plants and the substances needed for their growth.

It was a botanist (one who studies plants) called Sachs, who in the nineteenth century discovered information relating to the effects of different elements on plant growth. Non-metals necessary for the normal growth of a plant are carbon, hydrogen, nitrogen, phosphorus and sulphur. The principal metals required are potassium, calcium, magnesium, and iron. Modern methods of agriculture result in soils becoming short of some of these elements, and if the fertility of the soil is not to be reduced they must be replaced. This is the purpose of fertilizers and here the chemist comes to the aid of the farmer. Although four-fifths of the air is the vital element nitrogen, plants cannot make use of the gas directly. (The group of plants known as legumes is an exception). As indicated above, rain-water can introduce nitrogen, in the form of nitric acid, to the soil. This natural process does not provide enough nitrogen to replace that which is lost. The solution to the nitrogen problem was provided by the German chemist Haber, when he discovered a means by which the nitrogen of the air could be combined directly with hydrogen to form ammonia. Some of the ammonia is subsequently changed into nitric acid and the appropriate salts then prepared. This work indicates a close relationship between chemistry and biology which will be taken up later in the chapter.

### 4. Water

Just as rain-water carries nitric acid into the soil, water is needed to make fertilizers. This water has to be fresh water (ground water or surface water) and so the Sun's energy in evaporating water from the sea, and then being responsible for the movement of clouds towards the land once again assumes importance. This further fills out the statement that the Sun's energy makes life possible on Earth. To make 1 kg of fertilizer requires nearly 1000 litres of water. Other examples of industry's water requirements are the 200 litres or so required for 1 kg of steel, the 50 litres to refine 1 litre of petroleum, the 100 litres for 1 kg of cotton textiles and up to 1000 litres for 1 kg of rayon. These are facets of life in an industrial society, but every farmer operating even in the most primitive society knows that water is necessary for life.

The behaviour of water is quite unexpected, and the physicist and chemist have combined to find out all they can about this unusual substance. In contrast to most other liquids, water expands when it freezes. If this did not happen, lakes and rivers in the colder countries would turn to solid blocks of ice in winter making life impossible for fish. However, since ice is lighter than water, and both are poor conductors of heat, ice floats on the surface and prevents the lower layers of water from freezing.

Water freezes at 0°C and boils at 100°C and these are standard temperatures for thermometers. To make ice melt or water boil requires more heat than would be expected. As a result of this, clouds of water vapour carry a lot of heat from one place to another, so changing the weather. The behaviour of water at its surface makes it of prime importance in living

things — even man is about 65% water and he can be very uncomfortable if the lubricants, slippery films and sticky juices which support him become too thin or get too thick.

Chemistry deals with the composition of matter. Animal substance is a kind of matter and the modern chemist studies it as he would any other substance. Here he is overlapping with the biologist and in fact a new discipline known as biochemistry has grown up. One book asks the question 'Is Biology Chemistry?' On the other hand, following a revolution in scientific thinking at the beginning of this century chemistry could be considered as merged with physics. However, it is still possible to be a chemist, a biologist or physicist, but it is necessary to be aware that there are no hard and fast subject divisions. This study of our total environment is an example of crossing from one subject to another, the point being to show the wide variety of activity open to the chemist.

## 5. Conservation and pollution

When the environment is the subject of discussion, it is usually associated with the words conservation and pollution. Some comments about pollution have already been made in Chapters 4 and 5, but the purpose here is to look at it as a factor in the whole environment. The meaning of the environment has not, so far, been made clear. Dr Barry Commoner, a biologist, says it is the living things on Earth together with the air, water and soil in which they live. A narrower definition accepts it as a convenient word to cover all those things with which man comes into contact, and whose quality therefore determines the quality of human life. This second definition leads to a very personal idea of what pollution is. If one person is displeased, say, by a column of smoke rising from a fire, then that smoke is a pollutant. Or, to take another example, Man does not come into contact with the depths of the oceans and it could be said that these are suitable places for dumping waste. Obviously not everyone will agree with what is or is not polluting the environment so it is difficult to investigate the problem through the scientific method.

Dr Commoner's definition takes in features already discussed — air, sea and land and includes living things, so this leads to concern for plants and animals as well as Man himself. In normal circumstances the production of waste matter is at a level that can be dealt with by natural processes. For example, fish excrete waste which bacteria convert into substances required as food by algae and the algae are eaten by the fish so completing a cycle. Suppose sewage is allowed to escape into the river or sea. The amount of oxygen needed to support the conversion of the waste by the bacteria may be greater than the oxygen available in the water. The oxygen level is reduced to zero; lacking the necessary oxygen, the bacteria die and the sewage remains as an offence to eye and nose. The interference with this natural cycle constitutes pollution.

Another cycle is that which controls the amount of carbon dioxide in the atmosphere. The way in which this is done has already been mentioned in Chapter 4, but it will be repeated here in outline. Respiration and burning produce carbon dioxide and use up oxygen. This carbon dioxide is taken up by plants which then return oxygen to the atmosphere. What

happens if there are too many people filling the air with carbon dioxide? Supposing all the trees and plants are cut down? The first case would result in pollution owing to the lack of plant life to cope with all the extra carbon dioxide. In the second case, there would also be pollution, but the point is made to illustrate the need to consider conservation. In other words, it is unwise to cut down forests and to eliminate parks from cities, since these help to keep the air free from carbon dioxide as a pollutant. Forests need to be conserved for another reason and that is to prevent soil erosion. If the wind or rain takes the soil away, then there is nothing in which to grow the crops. It does not take long on the Earth's time scale for an area which was once covered with forest to become like the Sahara desert.

The natural order of things is made up of many cycles which normally continue undisturbed. It is human activity which is upsetting. In a sense Man is just another animal, consuming oxygen and food and producing carbon dioxide, heat and waste. Man has no environmental impact if he remains part of the cycle, which is the case, for example, if food is obtained from soil which receives the population's waste. If men are separated from the cycle by living in a city, their wastes are put into the surface water. The population is no longer part of the cycle involving the soil and the wastes intrude into the water cycle leading to water pollution.

The fact that the wastes are not returned to the soil disturbs that natural cycle and mention has already been made of the need to use fertilizers to make good the break in natural events. It is argued that the production of fertilizers is a misuse of resources which are limited in extent and that wise management demands conservation of the wealth of the Earth's crust. The alternatives to the high cost fertilizers are to make sure that human wastes are returned to the soil and to grow, say, one year in three, crops which will return nitrogen to the soil instead of removing it.

Pollution has had and is having disastrous effects whether it is viewed from the purely human standpoint of spoiling the quality of human life, or whether a more objective view is taken of the breakdown of natural cycles. That chemists around the world are concerned about this is shown by the fact that three of the monthly issues of *Chemistry in Britain* (the magazine of the Chemical Society and the Royal Institute of Chemistry), within a year, carried several full articles on the subject. Titles included 'Pollution of the Seas', 'The Threat to the Environment' and 'The Laws of environmental pollution'. With this knowledge of the damaging effects of pollution, each person has a responsibility to avoid adding any pollutant to air, sea or land. In addition, if human life is to have quality, then efforts must be made to conserve the character of our environment. A start with this can be made at the local level, even at school level as a group of students consider what is wrong and what can be done to improve the situation.

## Questions

1 What differences are noticed between the abundance of elements on Earth and on the Moon?

2  What evidence is there that leads you to suppose that the Universe contains the same elements as those discovered on Earth?

3  Outline a natural process by which nitrogen is returned to the soil.

4  'Is Biology Chemistry?' Try to work out an answer to this question for yourself.

5  Describe how a natural cycle could be upset by pollution.

6  Write notes on pollution as it affects your town or city.

7  Keep a scrap-book of newspaper and magazine items dealing with pollution.

# 8
# Matter and Change

IN the first section of this book, new words have been used to describe a variety of ideas associated with chemistry. In Chapter 1 the various changes of state were named. In Chapter 2, pure substances were introduced together with a description of the processes by which pure substances can be obtained. Chapter 3 went on to show that pure substances are either elements or compounds. This chapter looks again at pure substances as examples of matter and also considers some of the changes which matter can undergo.

An element has been defined as *a pure substance which cannot be split into anything simpler*. Chapter 3 gives information about many elements, which will not be repeated here. Attention is focussed on elements now, because if elements cannot be split into anything simpler, questions arise about the matter of which elements are made and what makes one element different from another.

## 1. Atoms

There is much evidence which indicates that matter is made up of very small particles. If the matter under consideration is an element, then these tiny particles are known as *atoms*. The picture, then, is that if one attempts to divide an element into smaller and smaller pieces, the process comes to end when a tiny indivisible particle is reached.

*An atom is the smallest particle of an element.*

The atom is indivisible and as originally thought of by John Dalton (remembered for his Atomic Theory put forward in 1803) all the atoms of the same element are identical. So, subject to a slight modification which will be introduced later on, an element is *a pure substance in which all the atoms are of one kind.*

## 2. Molecules

The other class of pure substances is that made up of compounds. Compounds consist of two or more elements combined together in such a way that their properties are changed. Dalton suggested the name 'compound atom' for the smallest particle of a compound, but the word that is used now is *molecule. A molecule is the smallest particle of a compound.* This is not the full meaning of 'molecule', since it has been found that even in elements the atoms are sometimes joined together in groups. For example,

the main gases of the air are oxygen and nitrogen which are elements; the smallest particles of these gases *occurring naturally* are not single atoms but pairs of atoms. 'Occurring naturally' is emphasized because it is only possible to get oxygen or nitrogen atoms under special conditions, but this does not mean that the definition of an atom has to be changed. The atom remains the smallest particle of an element which could be obtained, but when referring to normal conditions the word 'molecule' is used to name the smallest particle.

*The molecule is the smallest particle of a pure substance which can exist naturally.*

If the atoms in the molecules of a substance are all the same, then that substance is an element. If there are two or more kinds of atoms in the molecules, then the substance is a compound.



oxygen     hydrogen     nitrogen     carbon     phosphorus     sulphur

Fig. 8.1    **Dalton's Symbols for the Elements**

### 3. Chemical Symbols

In the history of chemistry many signs and symbols have been used to represent the substances under investigation. Dalton proposed the use of symbols to represent the atoms of different elements. Some of Dalton's symbols are shown in Fig. 8.1. With one hundred and five elements now known, Dalton's system would be very difficult to work with. Fortunately this is not necessary, because the Swedish chemist Berzelius who lived at the same time as Dalton, introduced the use of letters as symbols for the elements.

The simplest way of doing this, is to use the first letter of the name. For example, the letter O represents oxygen, and the letter H represents hydrogen. But there are only twenty-six letters in the alphabet so the names of several elements must begin with the same letter. For example, carbon, calcium, cadmium, chlorine, chromium, cobalt, copper. (There are actually eleven elements whose names begin with C). The second letter of the name is added to the first, or the first letter with another letter whose sound stands out when it is pronounced. Applying this to the elements listed above, the symbols become C, Ca, Cd, Cl, Cr, Co and then, strangely, Cu. Why Cu? In this case, the symbol is derived from the Latin name 'cuprum'. Other important symbols coming from Latin names are Fe — 'ferrum' (iron), Pb — 'plumbum' (lead), Ag — 'argentum' (silver). Some of the newer elements were given made-up Latin names. For example, sodium became 'natrium' and has the symbol Na, and potassium became 'kalium' and has the symbol K. It is important to note that the symbol of an element always has a capital letter and if there is a second letter it is always a small letter. It has been mentioned that the symbol is used to represent an element. In

the strictest sense this is not true because the symbol represents more precisely one atom of the element.

*The symbol of an element is one or two letters which represent one atom of the element.*

A list of common elements follows with the symbols representing one atom of the element.

| Metals | | Non-metals | |
|---|---|---|---|
| Element | Symbol for one atom | Element | Symbol for one atom |
| Potassium | K | Hydrogen | H |
| Sodium | Na | Chlorine | Cl |
| Calcium | Ca | Bromine | Br |
| Magnesium | Mg | Iodine | I |
| Aluminium | Al | Oxygen | O |
| Zinc | Zn | Sulphur | S |
| Iron | Fe | Nitrogen | N |
| Tin | Sn | Phosphorus | P |
| Lead | Pb | Carbon | C |
| Copper | Cu | Silicon | Si |
| Mercury | Hg | | |
| Silver | Ag | | |

Attention can now be turned to molecules. Molecules are represented by formulas which are written in such a way as to show the number of atoms of each element present in the molecule. The simplest formulas to write are those representing molecules of elements. The noble gases (helium, neon, argon, etc.) have single atoms as their smallest naturally existing particles. This is also true of the vapours of mercury and other metals. In these cases the atom is also the molecule, so, for example, 'He' represents both an atom and a molecule of helium.

The smallest particle of hydrogen which normally exists is a pair of atoms joined together, and the formula for this molecule is written $H_2$. This is not the same as writing 2H, which represents two free or uncombined atoms of hydrogen. In practical terms, atomic hydrogen is much more reactive than molecular hydrogen, so that to write 2H when $H_2$ is intended would be misleading.

The number of atoms in the molecule of an element is called its *atomicity*. Thus helium is *monatomic* and hydrogen is *diatomic*. If there are more than two atoms in the molecule of the element, then the element is

*polyatomic.* Atomicities of some elements are given in the following table:

| Element | Formula of Molecule | Atomicity |
|---|---|---|
| Helium | He | 1 |
| Neon | Ne | 1 |
| Hydrogen | $H_2$ | 2 |
| Nitrogen | $N_2$ | 2 |
| Oxygen | $O_2$ | 2 |
| Chlorine | $Cl_2$ | 2 |
| Bromine | $Br_2$ | 2 |
| Iodine | $I_2$ | 2 |
| Ozone | $O_3$ | 3 |
| Phosphorus | $P_4$ | 4 |
| Sulphur | $S_8$ | 8 |

*Notes:* 1. Ozone is not strictly an element, being the special name given to the form of oxygen having three atoms in the molecule.

2. Although $S_8$ is the correct molecular formula for sulphur, it is usual to use S for simplicity. This is also sometimes the case with phosphorus.

3. The term atomicity is applied only to elements.

## 4. Chemical Formulas

To represent molecules of compounds, the symbols of the atoms which are in combination are written next to one another. If there is more than one atom of a particular element, then a subscript is written after the atomic symbol in the same way as was done in writing the formulas of the molecules of polyatomic elements.

*Examples:*

(i)   Sodium chloride NaCl — this shows that the compound is derived from one atom of sodium and one atom of chlorine.

(ii)  Water $H_2O$ — two atoms of hydrogen combined with one of oxygen.

(iii) Potassium nitrate $KNO_3$ — 1 potassium, 1 nitrogen and 3 oxygen atoms combined together.

(iv)  Calcium carbonate $CaCO_3$ — 1 calcium, 1 carbon and 3 oxygen atoms combined.

(v)   Sulphuric acid $H_2SO_4$ — 2 hydrogen, 1 sulphur and 4 oxygen atoms combined.

*A formula represents the composition of a single molecule of an element or compound.*

Looking at a formula enables a chemist to tell immediately which elements are present in a compound, and also the amount of each element in terms of the number of atoms of each element in a single molecule. The formula does not give any indication of the way in which a compound is prepared. For example, although $H_2SO_4$ represents a molecule of sulphuric acid, this substance would not be obtained simply by putting two atoms of hydrogen, one of sulphur and four of oxygen together. In joining together to form compounds, the atoms of elements are changed, but it is still customary to interpret a formula by reference to the number of atoms of each element present. In your descriptions of your work in chemistry, you will refer to various compounds which may be made or taken from bottles on the shelves of a laboratory. The names of the compounds should be written in these descriptions, not formulas which only refer to single molecules. As with symbols, it may be convenient to write formulas in notes as a kind of shorthand.

## 5. Mixtures

If a substance has atoms which are all the same, then it is an element. If the molecules are all the same, it is either an element or a compound. If molecules are made up of only one kind of atom, then they are molecules of an element, but if there are two or more kinds of atoms, then they are molecules of a compound. Elements and compounds are the only pure substances, and if two or more kinds of molecules are present together in a substance it is a mixture.

*A mixture contains two or more substances which intermingle in any proportion without any chemical reaction having taken place.*

To make this statement clearer, work through the following series of experiments.
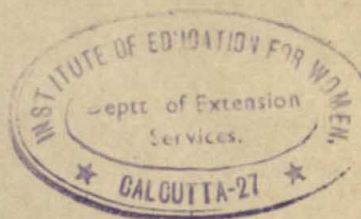
### EXPERIMENT 8.1   Properties of Iron and Sulphur

1. What is the colour of iron? of sulphur?

2. Bring a magnet close to the iron. What happens? What happens if the same thing is done to sulphur?

3. Warm some xylene in a test tube and add some iron. What happens? Repeat with sulphur. What happens?

4. Add dilute hydrochloric acid to each substance taken in test tubes. What do you see?

5. Put a light to the test tube from which gas is coming. What happens?

This experiment shows something of the properties of iron and sulphur which are summarized in the following table:

| Iron | Sulphur |
|---|---|
| Grey/black | Yellow |
| Attracted by magnet | Not attracted by magnet |
| Insoluble in warm xylene | Soluble in warm xylene |
| Reacts with dilute hydrochloric acid producing hydrogen. | Does not react with dilute hydrochloric acid |

## EXPERIMENT 8.2

1. Stir iron filings and powdered sulphur together. What happens?

2. Can you still see particles of iron and sulphur? Use a hand-lens to help you look more carefully. What is the colour?

3. Test the mixture in turn with a magnet, with warm xylene and with dilute hydrochloric acid, as in Experiment 8.1. Note what happens.

4. Does it make any difference how much iron and sulphur are mixed together?

## EXPERIMENT 8.3

1. Measuring by mass, take about twice as much iron as sulphur. Mix them together and put the mixture into a test tube until it is about one-third full.

2. Heat the mixture until it begins to glow. Remove the tube from the flame. What do you notice?

3. When the reaction has ceased and the tube cooled, break the tube and examine the product. What is its colour? What is the effect of a magnet, of xylene and of dilute hydrochloric acid on it?

## 6. Differences between mixtures and compounds

When the mixture in Experiment 8.3 was heated, the effect was clearly different from that achieved by simply stirring the elements together. The reaction between the two elements produced enough heat to keep itself going, and light was also produced. Not only was the type of change in Experiment 8.3 different from that in Experiment 8.2, the product also behaved differently. In Experiment 8.3, iron and sulphur have joined together chemically to form a compound — iron sulphide — and so a summary of results from these two experiments will help to sort out the differences between mixtures and compounds.

| Mixture: Iron and sulphur | Compound: Iron sulphide |
| --- | --- |
| Appearance depends on proportions of iron and sulphur. Individual grey and yellow particles can be seen. | Black and the same throughout. |
| Magnet lifts iron out of mixture; some sulphur may also come but this can be removed by shaking. | No effect (unless any iron remains unreacted). |
| Sulphur dissolves from mixture into warm xylene. | No effect. |
| Dilute hydrochloric acid produces hydrogen from the iron. | An entirely different gas called hydrogen sulphide with a smell of rotten eggs is produced. |

One clear result from these experiments is that in a mixture the components do not lose their identity, whereas they do in the compound. Also, making a mixture does not produce light or heat as was the case when the compound was formed. What is not directly apparent from these particular experiments is that while it is possible to mix iron and sulphur in all proportions, the amount of iron and sulphur in the compound is fixed. The differences between mixtures and compounds are summarized in the following table:

| Mixture | Compound |
| --- | --- |
| In a mixture the components may be present in any proportion. | The composition of a compound is fixed. |
| Mixtures are formed by physical changes, which can be reversed. | Formation involves chemical change, which is not normally reversible. |
| Components of a mixture keep their properties. | The properties of a compound are quite different from those of their component elements. |
| The components of a mixture can be separated by physical means. | The components of a compound can be separated by chemical change only. |

To help make the differences between compounds and mixtures clear, reference has been made to physical and chemical change. These terms have also been used in earlier chapters and it is now necessary to consider them in more detail.

## EXPERIMENT 8.4

Take small quantities of wood, coal, candle wax, iodine, copper sulphate crystals, powdered sulphur and red lead.

1. Put these substances into test tubes and heat gently.
2. Examine the substance carefully before and after heating.
3. If there is no apparent change heat the tube more strongly.
4. Hold a flame at the mouth of the test tubes to test for gases which burn.
5. Do any of the substances melt?
6. Are any of the substances the same after cooling as they were before heating?

## 7. Physical and Chemical Change

Coal and wood give off gases which burn. Wax melts and the iodine gives a purple gas, but both appear to turn back into the same substance on cooling. Copper sulphate crystals give off a substance which when it condenses on the cooler parts of the tube looks like water; white powder is left in the bottom of the tube. Red lead leaves a yellow substance and the flame may burn more brightly. The substances left behind in the wood and coal tubes look different from the original wood and coal.

The results of Experiment 8.4 show that heat can produce two types of change — there is a change of state when no new substances are produced, and there are those changes in which new substances are produced.

*A physical change is one in which no new substance is formed.*
*A chemical change is one in which one or more new substances are formed.*

Since substances are made up of molecules, a physical change represents no change in the atoms making up the molecules. In a chemical change the atoms have been rearranged into other molecules and hence new substances are formed. To help decide whether a change is physical or chemical, the differences between physical and chemical change are set out in the following table:

| Physical Change | Chemical Change |
|---|---|
| No new substance produced. | New substances produced. |
| Usually reversed by reversing the conditions. | Normally difficult to reverse. |
| Changes in heat energy usually small. | Usually accompanied by large changes in heat energy. |
| Chemical properties remain as before. | New chemical properties. |

## 8. Examples of Physical Change

(i) All changes of state are physical changes brought about by addition or removal of heat energy.

(ii) The passage of an electric current through copper wires or the filament of a lamp produces no new substance and the wire is unchanged when the current is switched off.

(iii) When a piece of iron is magnetized no new substance is formed. Hammering it or heating it will demagnetize it.

(iv) All mechanical changes, that is, changes of position, speed, state of division (lump or powder etc.), are physical in nature.

(v) The process of making a solution is usually considered to be a physical change, because it is easy to reverse by removing the solvent. Later, examples of solution will be given which are better considered as chemical changes.

## 9. Examples of Chemical Change

(i) When magnesium is heated in air, it burns with a brilliant white light leaving a white powder called magnesium oxide. This change can be represented as follows:

$$\text{Magnesium} + \text{oxygen} \longrightarrow \text{magnesium oxide}$$

or, making use of symbols and formulas

$$2Mg + O_2 \longrightarrow 2MgO.$$

This way of representing a chemical change is known as an *equation*. It is a convenient shorthand which has a number of uses. At this stage it will only be used as a shorthand, but a number of points must be made in this connection.

'2Mg' represents *two atoms of magnesium* (or two molecules since magnesium is monatomic).

'+' represents *reacts with*.

'$O_2$' represents *one molecule of oxygen*.

$\longrightarrow$  represents *producing*.

'2MgO' represents *two molecules of magnesium oxide*.

(Note that the 2 refers to the whole molecule; in one molecule there is one magnesium atom and one oxygen atom; there being two molecules formed means that two magnesium atoms and two oxygen atoms are involved).

A study of chemical changes has shown that atoms are not destroyed, so the number of atoms which react together must be the same as the number found in the products. This is why the phrase *chemical equation* is used, the number of atoms on the left of the arrow being equal to those on the right. This will be dealt with in much greater detail at a later stage.
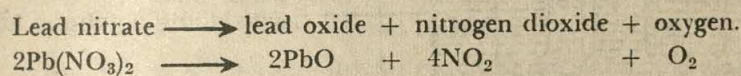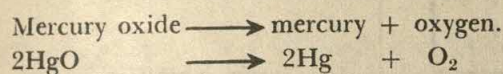
The reaction between magnesium and oxygen is an example of an *oxidation* reaction. It is also one example of *synthesis*, because a compound

has been made from its elements. The formation of iron sulphide already given in Experiment 8.3 is another example of synthesis.

Iron + sulphur ———→ iron sulphide.

$$Fe + S \longrightarrow FeS$$
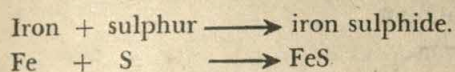
(ii) When studying elements and compounds in Chapter 3, mercury oxide and lead nitrate were heated so that they broke down into new substances. These are examples of *thermal decomposition*.

Mercury oxide ———→ mercury + oxygen.

$$2HgO \longrightarrow 2Hg + O_2$$

Lead nitrate ———→ lead oxide + nitrogen dioxide + oxygen.

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$

(iii) When silver nitrate solution is mixed with sodium chloride solution a white solid is formed which sinks slowly to the bottom of the test tube.

Silver nitrate + sodium chloride ———→ silver chloride + sodium nitrate

$$AgNO_3 + NaCl \longrightarrow AgCl \downarrow + NaNO_3$$
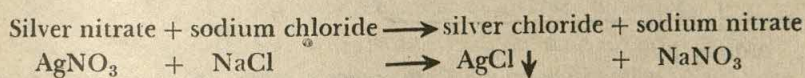
The solid formed when two solutions are mixed together is called a *precipitate* (represented by ↓) and the reaction is a *precipitation*.

(iv) When a small piece of zinc is placed in dilute sulphuric acid, bubbles are observed and the zinc eventually disappears. A lighted splint brought to the mouth of the test tube ignites the gas with a 'pop' showing the presence of hydrogen. If the solution remaining is evaporated, crystals of zinc sulphate are obtained. Often, it is loosely said that the zinc dissolves in the acid but clearly with new substances being produced this is not an example of the dissolving which is a physical change. The chemical change which has taken place is known as *displacement*, the zinc displacing the hydrogen from the acid.

Zinc + sulphuric acid ———→ zinc sulphate + hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$
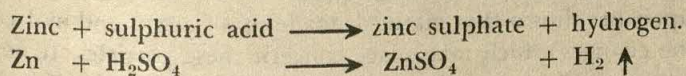
( ↑ indicates that a gas is evolved.)

In order to bring about or to speed up chemical changes, several agents are used. Commonly, heat energy is used as an agent of chemical change. This has been mentioned under thermal decomposition and also referred to in Experiment 8.4. It will be studied in more detail in the next chapter. Photography depends on chemical change brought about by light energy. One type of chemical change brought about by light is unwelcome as it causes colours to fade in curtains, carpets and clothing. The importance of plants to life has already been mentioned, and the chemical changes which are known as photosynthesis require the energy of sunlight to take place.

Experiment 8.5 gives one example of electrical energy in the form of an electric current bringing about chemical change.
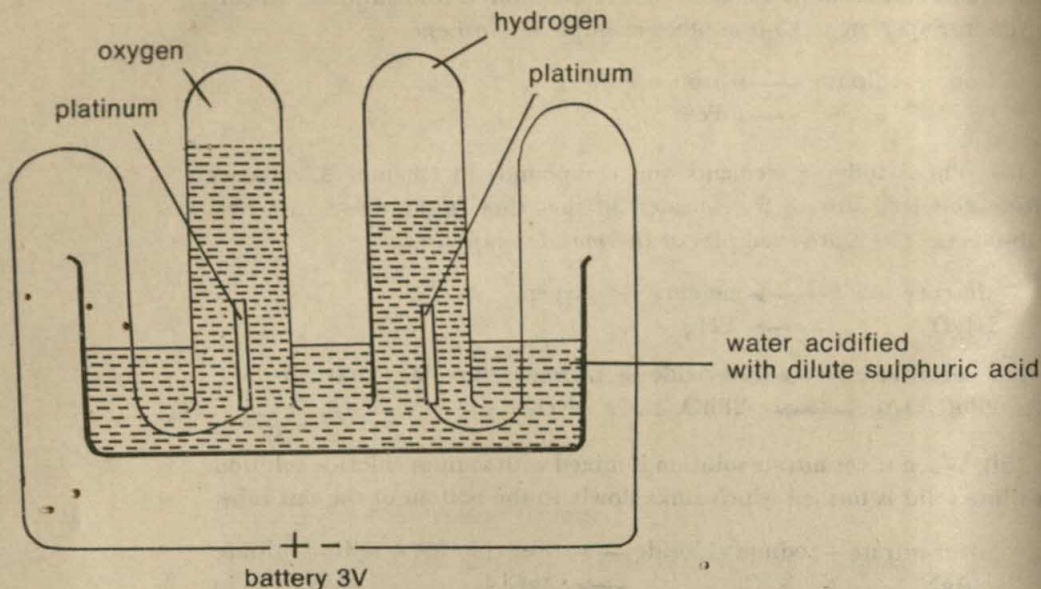
Fig. 8.2 Electricity as an Agent of Chemical Change

## EXPERIMENT 8.5

Set up an apparatus similar to that shown in Fig. 8.2. When the current is switched on, bubbles of gas will be seen to collect in the test tubes. The gases in each tube have been labelled, but how would you show that they are correct?

New substances are produced so this is a chemical change.

In Vol. III there is a chapter entitled 'Electricity as an agent of chemical change' which deals with this in more detail.

This chapter has shown that matter is made up of atoms and molecules and that the changes which take place concern these particles. If no re-arrangement takes place then the change is a physical change; if it does occur then the change is a chemical change. Heat, light and electrical energy can be used to bring about a chemical change.

### Questions

1  Distinguish between (a) an atom and a molecule (b) a symbol and a formula.

2  Write down the symbols for the following numbers of atoms:
(a) one of potassium (b) two of phosphorus (c) three of oxygen (d) four of carbon (e) five of chlorine (f) six of hydrogen (g) seven of oxygen (h) eight of nitrogen.

3 How many atoms are there in the following numbers of molecules?

(a) one of neon (b) two of sulphur (c) three of oxygen (d) four of phosphorus (e) five of oxygen (f) six of hydrogen.

4 Classify the following as element, mixture or compound:

(a) air (b) iron (c) brass (d) iron sulphide (e) chalk (f) ink (g) salt solution (h) water.

5 Give three differences between mixtures and compounds, by reference to iron, sulphur and iron sulphide.

6 Indicate three ways in which a chemical change differs from a physical change. State, with reasons, which of the following are chemical and which are physical changes:

(a) dissolving sodium chloride in water (b) the burning of magnesium in air (c) heating iodine (d) heating mercury oxide (e) precipitation.

7 Write down $C_{12}H_{22}O_{11}$ (representing a sucrose molecule).

a Draw a ring round a formula and a dotted line round a symbol.
b State how many atoms of each kind a molecule of sucrose contains.

8 Explain the difference between '$H_2$' and '2H'.

9 How many elements are known today? Why are Dalton's symbols not suitable to represent all these elements?

10 Fill in the blanks with suitable words:

a A substance whose atoms are alike is called an . . . . . .
b A substance whose atoms are not all alike, but whose molecules are all alike, is called a . . . . . .
c A substance whose molecules are not all alike is called a . . . . . .

11 Give an example, other than those given in the text, of a chemical change brought about by (a) heating (b) light (c) electricity.

# 9
# Heat as an Agent of Chemical Change

EARLIER chapters have shown that when substances are heated, a change occurs. The change may be temporary, or it may be permanent. Temporary changes have been mentioned in the last chapter, where they were referred to as physical changes. A physical change is only temporary because reversing the conditions reverses the change. Thus adding heat to water causes it to change state becoming steam. But as soon as the heat is removed, for example, by a cold surface, the steam condenses to water again. While these temporary changes are important to the chemist, particularly in separating mixtures and obtaining pure substances, they are less important when it comes to finding out what matter is made of. The chemist contributes to knowledge by finding out what makes up matter. One of the tools used for this is heat which brings about permanent changes in many substances. Heating substances can lead to the formation of new substances, that is to say, heat may bring about a chemical change.

Chapter 2 began with examples of heat causing permanent chemical change. Lead nitrate was heated and gave off a brown gas, a gas which relighted a glowing splint and a yellow powder was left behind. This information was used to show that the matter called lead nitrate, although a pure substance, could be decomposed into other pure substances. In Chapter 8 this reaction is given as an example of thermal decomposition — that is chemical change brought about by heat.

In this chapter, groups of substances will be heated to see if they undergo chemical change. The choice of substances has been made so that they can illustrate certain patterns. Looking for patterns among substances is part of the chemist's study of matter. Before carrying out the experiments which are given, one further point needs to be mentioned. All the substances to be heated are examples of the class of pure substances known as compounds.
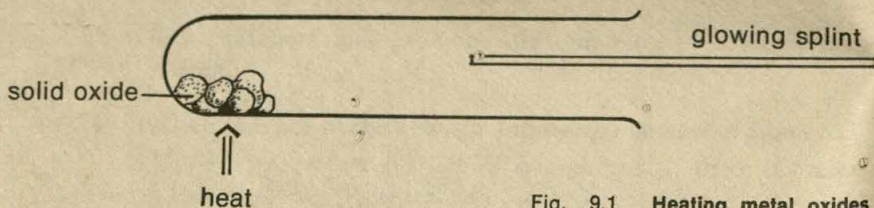


solid oxide

glowing splint

heat

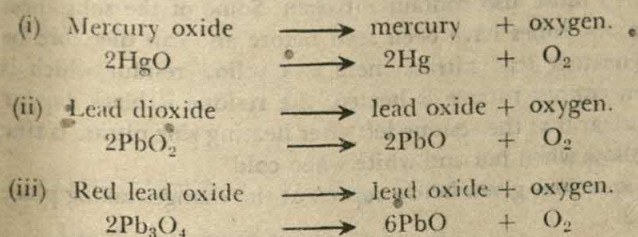Fig. 9.1 **Heating metal oxides**

## EXPERIMENT 9.1   Heating oxides

1. Use copper oxide, mercury oxide, zinc oxide, lead oxide, lead dioxide, red lead oxide, manganese dioxide.
2. Take a small quantity of the oxide and heat it strongly as shown in Fig. 9.1.
3. Put a glowing splint into the tube. Is oxygen being produced?
4. Note any changes in the appearance of the oxide. What happens on cooling?

The results for all seven oxides can be set down in a table as shown.

| Oxide | Change in appearance (if any) | Oxygen produced ($\checkmark$ Yes    $\times$ No) |
|---|---|---|
| Copper oxide | | |
| Mercury oxide | | |
| Zinc oxide | | |
| Lead oxide | | |
| Lead dioxide | | |
| Red lead oxide | | |
| Manganese dioxide | | |

The results of Experiment 9.1 fall into three groups. There are those oxides which apparently undergo no change on heating — copper oxide being an example. Other oxides such as mercury oxide and red lead oxide are permanently changed and the production of new substances, in particular oxygen, shows a chemical change to have occurred. The chemical changes brought about by heat in Experiment 9.1 can be represented by the following equations:

(i)   Mercury oxide $\longrightarrow$ mercury + oxygen.

$$2HgO \longrightarrow 2Hg + O_2$$

(ii)  Lead dioxide $\longrightarrow$ lead oxide + oxygen.

$$2PbO_2 \longrightarrow 2PbO + O_2$$

(iii) Red lead oxide $\longrightarrow$ lead oxide + oxygen.

$$2Pb_3O_4 \longrightarrow 6PbO + O_2$$

Zinc oxide does not produce any new substance on heating but it does go yellow, only to become white again on cooling. This, then, is an example of a temporary physical change. This feature of zinc oxide should be noted since it helps in detecting the presence of zinc in substances. The chemist

often has to do some detection work when given unknown substances. If all the seven substances in Experiment 9.1 were unknown, then the results would show that some, at least, contain oxygen because it is driven off when they are heated. This does not mean, however, that the others do not. The fact that heating did not bring about a chemical change, releasing oxygen, does not establish that. Experiments 9.2 and 9.3 will show how other deductions can be made.
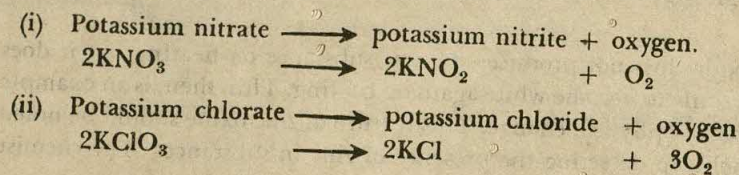
## EXPERIMENT 9.2

The procedure is the same as in Experiment 9.1, but different substances are to be heated. Take potassium nitrate, potassium chlorate, potassium permanganate, lead nitrate, copper nitrate, and zinc nitrate. The changes are more complicated than in Experiment 9.1, so more care must be taken in observing them.

Enter the results in the following table:

| Compound | Change in appearance | Gases produced |
|---|---|---|
| Potassium nitrate | | |
| Potassium chlorate | | |
| Potassium permanganate | | |
| Lead nitrate | | |
| Copper nitrate | | |
| Zinc nitrate | | |

In Experiment 9.2, heat produces a chemical change in all cases, because new substances are produced. The most obvious product is the brown gas which has already been identified as nitrogen dioxide. Oxygen is obtained from the heating of all these compounds, so they must all contain oxygen. Nitrogen dioxide contains nitrogen, and so those compounds from which this gas is obtained must also contain nitrogen. Some of the substances remaining in the test tubes have been seen before and can therefore be identified. After heating lead nitrate there is a yellow residue which is lead oxide. When copper nitrate is heated, the residue is black copper oxide. It is fairly clear that the residue left after heating zinc nitrate is zinc oxide, it being yellow when hot and white when cold.

The chemical equations given below represent the changes taking place in Experiment 9.2.

(i) Potassium nitrate $\longrightarrow$ potassium nitrite + oxygen.

$2KNO_3 \longrightarrow 2KNO_2 \qquad + O_2$

(ii) Potassium chlorate $\longrightarrow$ potassium chloride + oxygen

$2KClO_3 \longrightarrow 2KCl \qquad + 3O_2$

(iii) Potassium permanganate $\longrightarrow$ potassium manganate + manganese dioxide + oxygen.

$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

(iv) Lead nitrate $\longrightarrow$ lead oxide + nitrogen dioxide + oxygen.

$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$

(v) Copper nitrate $\longrightarrow$ copper oxide + nitrogen dioxide + oxygen.

$2Cu(NO_3)_2 \longrightarrow 2CuO + 4NO_2 + O_2$

(vi) Zinc nitrate $\longrightarrow$ zinc oxide + nitrogen dioxide + oxygen.

$2Zn(NO_3)_2 \longrightarrow 2ZnO + 4NO_2 + O_2$

In Experiment 9.2, four different nitrates were heated. The fact that the word 'nitrate' occurs in all the names, should make you think that they have something in common. Look at the molecular formulas to see if you can find what is common to them all. In Experiment 9.3 another group of compounds called carbonates is heated. Again, looking at the formulas will reveal the same group of atoms in all of the formulas.
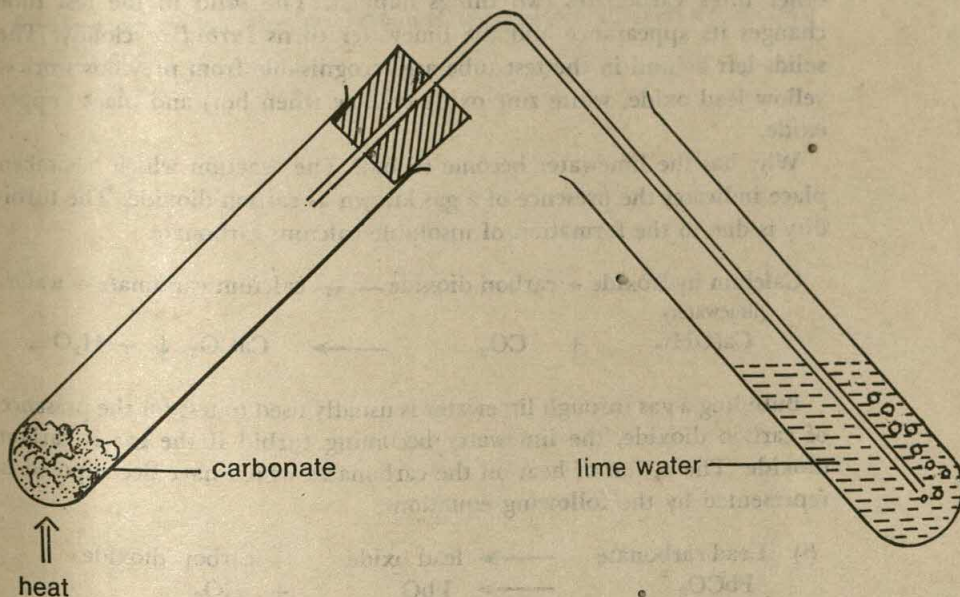


Fig. 9.2  Action of heat on carbonates

## EXPERIMENT 9.3  Heating carbonates

1. Use the apparatus shown in Fig. 9.2.

2. Heat the following carbonates: (i) lead, (ii) zinc, (iii) calcium, (iv) copper and (v) sodium.

3. Look for changes in the appearance of the solid being heated.

4. What happens to the limewater?

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Put the results into a table as shown below:

| Solid | Appearance of solid | | Change in appearance of limewater (√ Yes    × No) |
| --- | --- | --- | --- |
| | Before heating | After heating | |
| Lead carbonate | | | |
| Zinc carbonate | | | |
| Calcium carbonate | | | |
| Copper carbonate | | | |
| Sodium carbonate | | | |

The first thing that emerges from this experiment is that heating calcium carbonate and sodium carbonate produces no apparent change. With the other three carbonates two things happen. The solid in the test tube changes its appearance and the limewater turns *turbid* or cloudy. The solids left behind in the test tube are recognisable from previous work – yellow lead oxide, white zinc oxide (yellow when hot) and black copper oxide.

Why has the limewater become turbid? The reaction which has taken place indicates the presence of a gas known as carbon dioxide. The turbidity is due to the formation of insoluble calcium carbonate.

Calcium hydroxide + carbon dioxide $\longrightarrow$ calcium carbonate + water.
(limewater)
$$Ca(OH)_2 \quad + \quad CO_2 \quad \longrightarrow \quad CaCO_3 \downarrow + H_2O$$
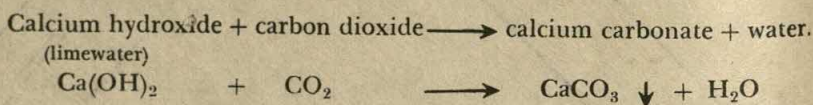
Bubbling a gas through limewater is usually used to test for the presence of carbon dioxide, the limewater becoming turbid if the gas is carbon dioxide. The action of heat on the carbonates which have decomposed is represented by the following equations:

(i) Lead carbonate $\longrightarrow$ lead oxide + carbon dioxide.
$$PbCO_3 \longrightarrow PbO + CO_2.$$

(ii) Zinc carbonate $\longrightarrow$ zinc oxide + carbon dioxide.
$$ZnCO_3 \longrightarrow ZnO + CO_2$$

(iii) Copper carbonate $\longrightarrow$ copper oxide + carbon dioxide.
$$CuCO_3 \longrightarrow CuO + CO_2$$
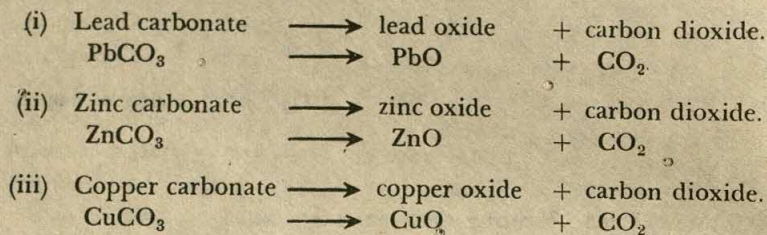
Experiments 9.1, 9.2 and 9.3 all show heat as an agent of chemical change, since in all three experiments new substances were produced. Of these new substances, oxygen will be studied in Chapter 10 and carbon dioxide in Chapter 11. The oxides of the metals will be a subject of study at a later stage.

## Questions

1  Describe and explain what happens when each of the following substances is heated strongly in a test tube: (*a*) zinc oxide (*b*) red lead oxide (*c*) potassium chlorate (*d*) copper carbonate.

2  Mercury is an element and mercury oxide is a compound. What is meant by this statement? Describe how you could get mercury and oxygen from mercury oxide.

3  When you blow through limewater, it soon becomes turbid, but this does not happen if the air you breathe in is first passed through lime-water. Can you suggest an explanation for this?

4  A white solid when heated turns yellow and gives off a gas which turns limewater turbid. When the solid remaining in the test tube cools, it is white. Identify the original solid and explain the observations.

5  Why is thermal decomposition an example of chemical change?

6  How can we test whether oxygen is being given off when a substance is heated?

# 10
# Oxygen

## 1. Natural occurrence of oxygen

OXYGEN is the most abundant of all the elements. As such it has been spoken of in a number of chapters already. Oxygen is found in the air, the sea and the land. In the air, oxygen is mostly present as the uncombined element, occupying one-fifth of the total volume. Some oxygen is dissolved in the water of the sea, providing fish and other organisms in the sea with one of their means of life. This uncombined oxygen does not account for much of the total oxygen which exists. Most oxygen is combined with other elements in a wide variety of compounds. Water contains nearly 89% of oxygen by weight, and oxygen is one of the elements present in most of the rocks and minerals of the Earth's crust.

Oxygen has been shown to be necessary for burning and respiration, being the part of the air which is used up by these processes. In Chapter 9, oxygen was shown to be present in a number of compounds, from which it could be obtained by heating. All of these substances could be used as a source of oxygen, but, for a number of reasons, they are not normally used.

## 2. Laboratory sources of oxygen

Mercury oxide, used by Scheele and Priestley as a source of oxygen, is expensive. Other substances such as lead dioxide, red lead oxide and potassium nitrate do not give as much oxygen as other substances which are readily available. When the other nitrates are heated, oxygen is produced, but so also is nitrogen dioxide so that a separation of the two gases would be necessary to get the oxygen. This leaves potassium chlorate and this has long been used as the laboratory source of oxygen although not normally by itself. If potassium chlorate is heated alone, it melts and then decomposes. When manganese dioxide is added to potassium chlorate (about one-fifth of the total weight being manganese dioxide), oxygen is given off at a much lower temperature, 200°C instead of about 600°C, and at a steadier rate. The reaction is:

$$\text{Potassium chlorate} \longrightarrow \text{potassium chloride} + \text{oxygen.}$$
$$2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$$
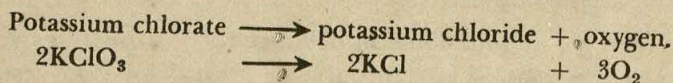
Notice that no mention is made of manganese dioxide in the equation. Why is this? From Experiment 9.1, we would not expect it to release its

oxygen, but it must make some contribution to the decomposition of potassium chlorate as that reaction goes faster in the presence of manganese dioxide. However, if water is added to the test tube after it has cooled to dissolve the potassium chloride and the solution filtered, black manganese dioxide is collected in the filter paper. When this has been washed and dried, the amount of manganese dioxide is found to be the same as at the beginning. So, in some way the manganese dioxide makes the potassium chlorate give up its oxygen more readily but is itself the same at the end as at the beginning. Manganese dioxide is not the only substance to act in this way; copper oxide and ferric oxide (an oxide of iron) will also help potassium chlorate to give up its oxygen more readily. These substances are known as *catalysts*.

*A catalyst is a substance which increases the rate of a chemical change, without itself undergoing any permanent chemical change.*

This discussion of potassium chlorate has been given because of its link with Chapter 9. However, explosions causing serious injuries have resulted from the heating of the potassium chlorate/manganese dioxide mixture. This has been due to using impure manganese dioxide containing carbon or mistakenly using charcoal itself. Thus, the method given in Experiment 10.1 is recommended for the laboratory preparation of oxygen.
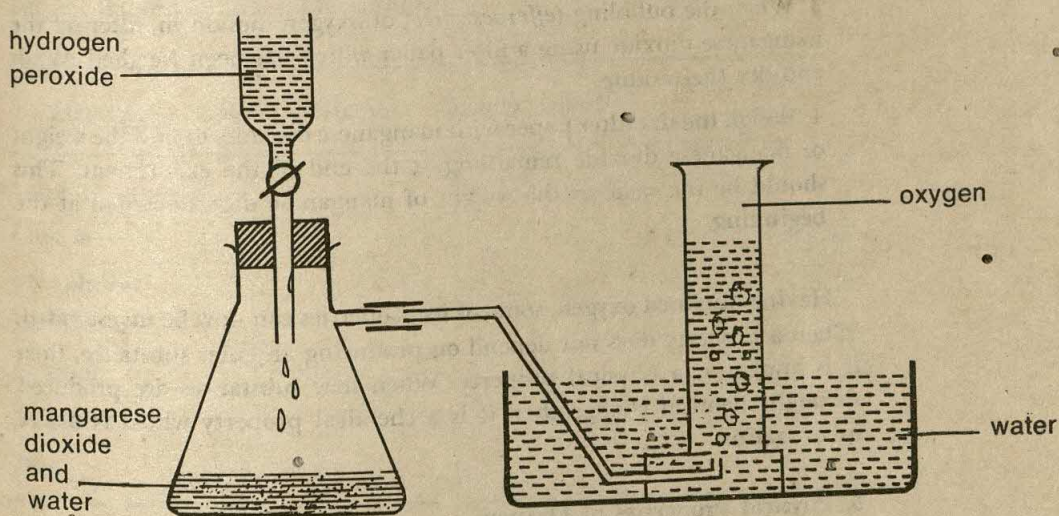


Fig. 10.1   Preparation of Oxygen

## EXPERIMENT 10.1   Preparation of oxygen

1. Set up the apparatus as shown in Fig. 10.1.
2. Drop hydrogen peroxide into the flask containing manganese dioxide dispersed in a little water.

3. Let the first bubbles of gas escape and then turn a gas jar full of water upside down over the beehive shelf.

4. When the water in the jar has been displaced by oxygen, slide a greased glass cover over its mouth underwater. Fill several gas jars in this way for use in Experiment 10.3.

The equation for the reaction in Experiment 10.1 is written as:

$$\text{Hydrogen peroxide} \longrightarrow \text{water} + \text{oxygen.}$$
$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
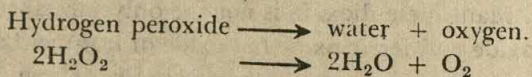
Notice, once again, that although manganese dioxide is present, it is not written in the equation. This is another example of *catalysis*, the process in which a catalyst speeds up a chemical reaction. That manganese dioxide acts as a catalyst for the decomposition of hydrogen peroxide is shown by Experiment 10.2.

## EXPERIMENT 10.2

1. Take two test tubes and half-fill each of them with hydrogen peroxide. Look closely for any bubbles of gas.

2. Put a weighed amount of manganese dioxide into one of the tubes. What change takes place in the bubbling of gas from this tube?

3. When the bubbling (*effervescence*) of oxygen dies down, filter off the manganese dioxide using a filter paper which has been weighed. Wash and dry the residue.

4. Weigh the dry filter paper with manganese dioxide, to find the weight of manganese dioxide remaining at the end of the experiment. This should be the same as the weight of manganese dioxide added at the beginning.

Having obtained oxygen, some of its properties can now be investigated. When a property does not depend on producing any new substance, then it is known as a physical property. When new substances are produced through chemical change then it is a chemical property which is under investigation.

## 3. Physical Properties of Oxygen

Oxygen is a gas which is colourless and has no smell. It is not very soluble in water.

## 4. Chemical Properties of Oxygen

Oxygen itself does not burn, but is essential to the burning of all other substances. Experiment 10.3 describes the burning of a number of different elements in oxygen.

## EXPERIMENT 10.3

1. Warm some sulphur in a deflagrating spoon until it begins to burn. and then plunge the burning sulphur into a gas jar of oxygen. Make a note of the colour of the flame. When the reaction ceases, add a little water, put back the glass cover and shake the jar and its contents. Add a few drops of neutral litmus solution and notice the colour change, if any.

2. Put a small piece of phosphorus in a deflagrating spoon into a gas jar of oxygen. What happens? The other steps are the same as those described for sulphur.

3. Carbon in the form of charcoal must be heated until it begins to glow, before it is plunged into the gas jar of oxygen. Then proceed as before.

4. Heat a small piece of sodium in a deflagrating spoon until it melts and then plunge it into a gas jar of oxygen.

5. Heat a piece of calcium strongly and when it ignites plunge it into a gas jar of oxygen. Do the same thing with a piece of magnesium ribbon.

6. As a source of iron, use steel wool and heat to redness before plunging it into a gas jar of oxygen.

In 3, 4, 5, and 6, note the colour of the flame, if any, and proceed as in 1 when the reaction has ceased.



Fig. 10.2   **Burning Elements in Oxygen**

Set out the results in a table as shown.

| Element | Colour of flame | Litmus colour | Metal or non-metal |
|---|---|---|---|
| Sulphur | | | |
| Carbon | | | |
| Phosphorus | | | |
| Sodium | | | |
| Calcium | | | |
| Magnesium | | | |
| Iron | | | |

Equations for the reactions taking place in Experiment 10.3 are written here for completeness, although some of them raise difficulties which cannot be taken up at this stage.

*Sulphur:*    Sulphur    + oxygen $\longrightarrow$ sulphur dioxide.
              S         + $O_2$   $\longrightarrow$ $SO_2$

*Phosphorus:* Phosphorus + oxygen $\longrightarrow$ phosphorus pentoxide.
              $P_4$      + $5O_2$  $\longrightarrow$ $P_4O_{10}$

63
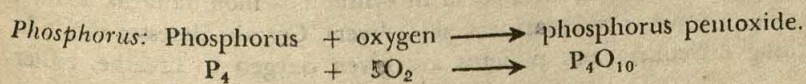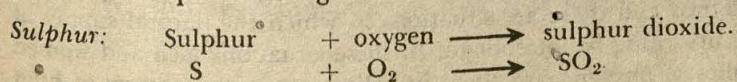
| Carbon: | Carbon | + oxygen | $\longrightarrow$ | carbon dioxide. |
| | C | + $O_2$ | $\longrightarrow$ | $CO_2$ |
| Sodium: | Sodium | + oxygen | $\longrightarrow$ | sodium peroxide. |
| | $2Na$ | + $O_2$ | $\longrightarrow$ | $Na_2O_2$ |
| Calcium: | Calcium | + oxygen | $\longrightarrow$ | calcium oxide. |
| | $2Ca$ | + $O_2$ | $\longrightarrow$ | $2CaO$ |
| Magnesium: | Magnesium | + oxygen | $\longrightarrow$ | magnesium oxide. |
| | $2Mg$ | + $O_2$ | $\longrightarrow$ | $2MgO$ |
| Iron: | Iron | + oxygen | $\longrightarrow$ | magnetic iron oxide. |
| | $3Fe$ | + $2O_2$ | $\longrightarrow$ | $Fe_3O_4$ |

The classification of elements into metals and non-metals on the basis of physical properties was mentioned in Chapter 3. In Chapter 8 a list of metals and non-metals was given, so the last column in the above table can be filled in by reference to that list if necessary. The results of Experiment 10.3 give a chemical property by which it might be possible to distinguish between metals and non-metals. Solutions of the products of burning i.e. solutions of the oxides of the elements, turn the neutral litmus red or blue. No change is observed in the case of iron because the oxide in this case is insoluble in water. The non-metal oxide solutions turn litmus red and the metal oxide solutions turn litmus blue. Litmus is known as an *indicator*. When it turns red it indicates an *acidic* solution and when it turns blue it indicates an *alkaline* solution. Acidic and alkaline solutions will be considered in greater detail next year. At this stage an acidic solution can be regarded as one which turns litmus red and an alkaline solution as one which turns litmus blue.

A general statement can now be made about metals and non-metals. Metal oxides, when soluble, give alkaline solutions. Non-metal oxides, when soluble, give acidic solutions. To group together metal oxides, whether soluble or not, the term *basic oxide* is used. Non-metal oxides which give acidic solutions are known as *acidic oxides*.

## 5. Uses of oxygen

To prepare oxygen in the laboratory, an oxygen-containing compound has been decomposed. With so much elemental oxygen in the air, it would be surprising if this were overlooked as a source when oxygen is required on a large scale. The details of separating oxygen from the other gases of the air will have to wait. The important thing is that it is done and the world produces about six million *tonnes* of oxygen a year. About 80% of this manufactured oxygen is used in the production of iron and steel. The importance of this is indicated by the fact that more iron is used than all the other metals put together. The necessity of oxygen for life has already been mentioned and there are situations in which the natural supply of oxygen for breathing is not enough. In these situations men and women carry supplies of oxygen with them in cylinders — mountaineers at high altitudes, astronauts, submariners, skin divers. Certain illnesses result in breathing difficulties and patients are given oxygen to breathe, either

through a mask or by being put in an oxygen tent. Another medical use of oxygen is when an anaesthetic is used to make a patient unconscious. The anaesthetic must be mixed with oxygen to keep the patient alive. A feature of burning is the release of heat energy. In the case of some gases very hot flames are produced. For example, the gas acetylene mixed with oxygen and burned gives a flame which can cut steel over 30 cm thick, the temperature being about 3000°C — this is known as the oxy-acetylene flame. In the large rockets used, for example, in the Apollo space missions, liquid oxygen is carried in tanks to provide the oxygen which the fuel needs to burn in. Saturn 5 rockets use kerosene as the fuel in stage 1; stages 2 and 3 burn hydrogen in oxygen.

## Questions

1 Write in words and formulas the equation for the decomposition of
   a potassium chlorate
   b hydrogen peroxide.

2 Why would you prefer not to use potassium chlorate mixed with manganese dioxide as a source of oxygen?

3 What are two essential points about a catalyst?

4 Under what conditions does oxygen react with (a) phosphorus, (b) sulphur (c) sodium (d) magnesium? Describe what you see when the reactions take place and name the products.

5 Write in words and symbols the equation for a reaction
   a which makes sulphur dioxide
   b of oxygen with magnesium.

6 Explain, with examples, the meanings of acidic oxide and basic oxide. How would you obtain an alkaline solution from the burning of a suitable substance?

7 Summarize the last paragraph of this chapter by making a list of the uses of oxygen.
   Can you find out any other uses which have not been mentioned?

8 Name three abundantly occurring substances which contain oxygen.

9 Explain the use of oxygen in (a) hospitals (b) shipyards (c) mountaineering (d) rocket propulsion.

10 Which physical property of oxygen is important to marine life? Explain why.

# 11
# Carbon Dioxide

## 1. Natural occurrence of carbon dioxide

INFORMATION about carbon dioxide has been given in a number of places in preceding chapters. Carbon dioxide is one of the gases present in the air mixture, to the extent of about 0.03%. This figure remains about the same although carbon dioxide is constantly added to the air by respiration and burning, because the gas is taken up by plants during the process of photosynthesis. When some carbonates are heated, carbon dioxide is one of the products and it is also obtained when carbon (in the form of charcoal) is burned in oxygen. Carbon dioxide is an acidic oxide, its solution turning litmus red. When carbon dioxide is bubbled through limewater, the limewater turns turbid.

## 2. Laboratory sources of carbon dioxide

Natural processes have been producing carbon dioxide since the beginning of time, but since it is normally a gas, its laboratory preparation was delayed until the time of Van Helmont. Another century went by until a Scottish chemist, Joseph Black, prepared and examined it, showing it to be a new gas. One of his methods of preparation was to heat magnesium carbonate:

$$\text{Magnesium carbonate} \longrightarrow \text{magnesium oxide} + \text{carbon dioxide}$$
$$MgCO_3 \longrightarrow MgO + CO_2 \uparrow$$
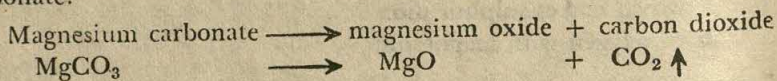
Another method is described in Experiment 11.1.



dilute hydrochloric acid

carbon dioxide

marble chips

collecting a gas by 'downward delivery'
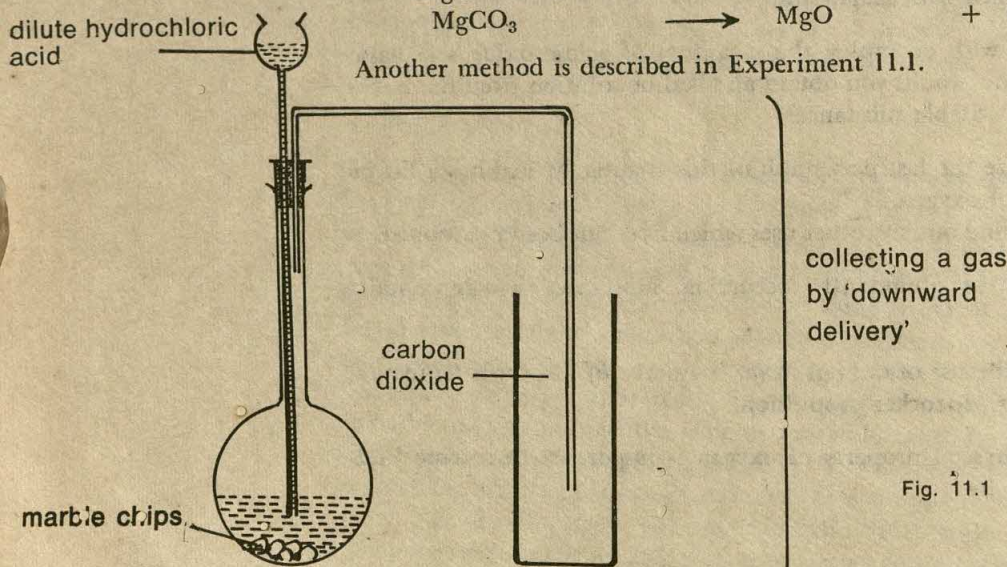
Fig. 11.1  Preparation of Carbon Dioxide

## EXPERIMENT 11.1  Preparation of carbon dioxide

1. Set up the apparatus as shown in Fig. 11.1.

2. Pour dilute hydrochloric acid (a solution of the gas hydrogen chloride in water) down the thistle funnel onto lumps of marble in the bottom of the flask.

3. Collect the gas by downward delivery. (This means that the gas falls to the bottom of the gas jar while the air that was originally in the jar floats upwards on top of the carbon dioxide).

4. Put a lighted splint in the top of the gas jar. When the gas jar is full, this will go out.

5. Put a cover over the full gas jar and fill several others in the same way.

The equation for this reaction can be written as:

Calcium carbonate + hydrochloric acid ⟶ calcium chloride + water + carbon dioxide

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$
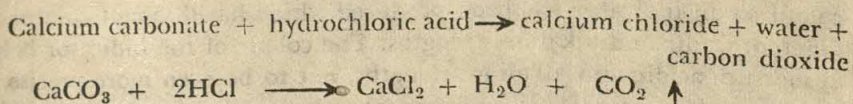
## 3. Physical properties of carbon dioxide

Studying the preparation and collection of carbon dioxide, shows some of its physical properties. It is a colourless gas without a smell and it is denser than air.

## EXPERIMENT 11.2

1. Take a gas jar of carbon dioxide and pour it into a beaker with a lighted candle standing in it. (See Fig. 11.2). What happens?

2. Which property of carbon dioxide does this experiment illustrate?

Having discovered that carbon dioxide is denser than air, it is reasonable to ask why the Earth's surface is not covered with a blanket of carbon dioxide. In normal conditions the movements of the molecules of all the gases of the air keep these gases mixed together. But there are some places where carbon dioxide actually comes up from the Earth and collects in caves, mines and dry wells. One place in Java is known as Poison Valley and it is littered with the bones of small animals. Carbon dioxide is not in fact poisonous; death occurs because the animals, being surrounded by carbon dioxide, are starved of oxygen.

If the temperature is below $31°C$, an increase in pressure will turn the gas into liquid. A sudden release of pressure results in the temperature falling to $-78°C$ and solid carbon dioxide is formed. Liquid carbon dioxide only exists at pressures greater than atmospheric, so solid carbon dioxide normally passes direct to the gas state when it warms up — an example of sublimation.

Carbon dioxide is soluble in water to the extent that one volume of water dissolves an equal volume of carbon dioxide at room temperature.



air out
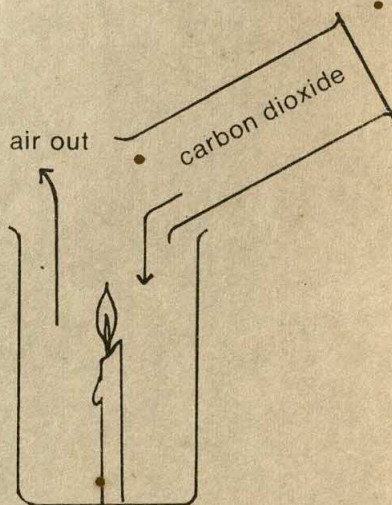
carbon dioxide

Fig. 11.2    **Pouring Carbon Dioxide**

If the pressure is increased, the solubility increases and this is done in making soda-water and all related fizzy drinks. Opening a bottle of fizzy drink releases the pressure so that bubbles of carbon dioxide are seen to escape.

## 4. The pH scale

In Experiment 10.3, litmus was used to show whether a solution was acidic or alkaline. The litmus turns red in acidic solution and blue in alkaline solution. Some difference may have been observed between the red colour of sulphur dioxide solution and that of the carbon dioxide solution. Whether or not this difference was seen, it may not have been considered as significant. The point is, however, that there are degrees of strength of both acidic and basic solutions. For example, one acidic solution can be stronger or weaker than another and the slight difference in the red of the litmus is an indication of this. But it is not easy to see shades of the same colour so an indicator has been produced which has different colours at different acidic and alkaline strengths. The colour of the indicator helps to measure acidic and alkaline strengths, but to be even more precise, a number scale is used. This number scale which tells how strongly acidic or alkaline a solution is, is called the 'pH scale'. The indicator which shows pH values by its colour is known as *Universal indicator*. The colours corresponding to different pH values are shown on the bottle containing the indicator. These might, for example, be those given below:

| ACIDIC | | NEUTRAL | | | ALKALINE | |
|---|---|---|---|---|---|---|
| Red | Orange | Yellow | Green | Blue | Indigo | Violet |
| 1-4 | 5 | 6 | 7 | 8 | 9 | 10-14 |

The lower the pH number the more acidic the solution, and the higher the number, the more alkaline it is.

## 5. Chemical properties of carbon dioxide

In Experiment 11.3, a number of reactions are carried out in order to discover the chemical properties of carbon dioxide.

### EXPERIMENT 11.3

1. Add some water to a gas jar of carbon dioxide and shake for a few minutes. Test the solution with Universal Indicator and find out the pH represented by the colour obtained.

2. Bubble carbon dioxide through limewater until no further change takes place. Note the changes which occur. Boil the solution and again note what happens.

3. Take sodium hydroxide solution and add a few drops of Universal indicator. Bubble carbon dioxide through the solution until the indicator is green, noting the changes of colour which occur before the green appears.

4. Ignite a piece of magnesium ribbon about 10 cm long and plunge it into a gas jar of carbon dioxide. When the reaction has finished see if

you can identify two different solids. What happens when dilute sulphuric acid is shaken up with the products?

By section 1 of Experiment 11.3, we are reminded that carbon dioxide is an acidic oxide, although the indicator shows its solution to be only weakly acidic. Limewater and sodium hydroxide solution are both alkaline solutions and sections 2 and 3 of Experiment 11.3 show what happens when acidic and alkaline solutions react together. This is clearer with limewater because the first product is insoluble, being calcium carbonate. The reaction is:

Calcium hydroxide + carbon dioxide $\longrightarrow$ calcium carbonate + water
(limewater)

$$Ca(OH)_2 \quad + \quad CO_2 \quad \longrightarrow \quad CaCO_3 \downarrow \quad + H_2O$$
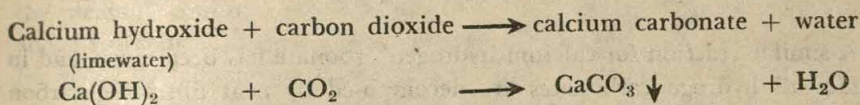
When the turbidity disappears, a further reaction has taken place producing a soluble substance — calcium hydrogencarbonate (calcium bicarbonate).

Calcium carbonate + water + carbon dioxide $\longrightarrow$ calcium hydrogen-carbonate

$$CaCO_3 \quad + H_2O + \quad CO_2 \quad \longrightarrow \quad Ca(HCO_3)_2$$
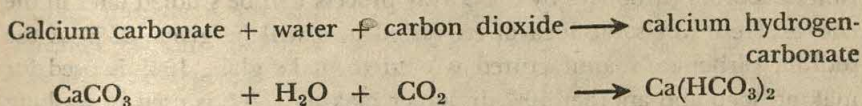
Rain-water contains carbon dioxide dissolved in it, so that the weathering of rocks containing calcium carbonate (e.g. chalk, limestone, marble) is a natural example of the above reaction. It also represents a way in which calcium enters the water supply. This is important as a source of calcium for building bones, but it also results in water which does not easily give a lather with soap — this is an example of *hard water* which will be discussed in the chapter on water.

Boiling the solution of calcium hydrogencarbonate results in the formation of calcium carbonate again.

Calcium hydrogencarbonate $\longrightarrow$ calcium carbonate + water + carbon dioxide

$$Ca(HCO_3)_2 \quad \longrightarrow \quad CaCO_3 \quad + H_2O + CO_2 \uparrow$$
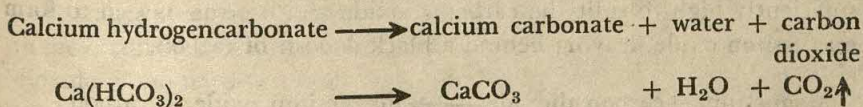
This indicates that if hard water containing calcium hydrogencarbonate is boiled, then the calcium is removed in the form of insoluble calcium carbonate.

The same reactions occur with sodium hydroxide. The indicator is used to show that the acidic oxide neutralizes the effect of the alkaline solution. The green colour is taken as a convenient stopping point, because in fact the reaction is complete before that point is reached. The reactions taking place are:

Sodium hydroxide + carbon dioxide $\longrightarrow$ sodium carbonate + water

$$2NaOH \quad + \quad CO_2 \quad \longrightarrow \quad Na_2CO_3 \quad + \quad H_2O$$

Sodium carbonate + water + carbon dioxide $\longrightarrow$ sodium hydrogen-carbonate

$$Na_2CO_3 \quad + H_2O + \quad CO_2 \quad \longrightarrow \quad 2NaHCO_3$$
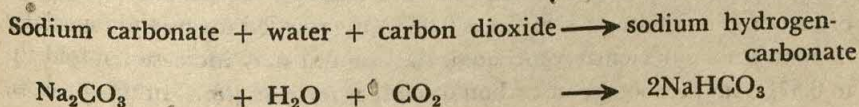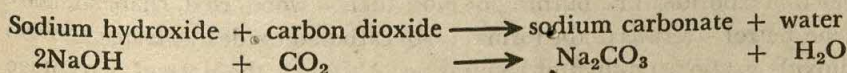
If the sodium hydroxide solution were concentrated, then sodium hydrogencarbonate would be precipitated. This is important industrially because, in the manufacture of sodium carbonate, the reactions proceed to the formation of sodium hydrogencarbonate which is filtered off. Some of the sodium hydrogencarbonate is used as 'bicarbonate of soda' or 'baking soda', and it is a constituent of baking powder. Its use in baking depends on the fact that when heated it decomposes giving off carbon dioxide.

Sodium hydrogencarbonate $\longrightarrow$ sodium carbonate + water + carbon dioxide

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$
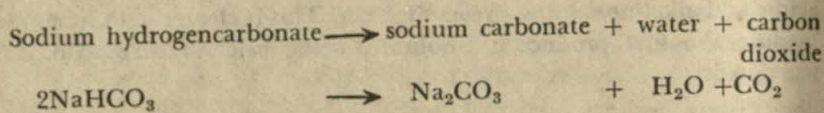
A similar reaction for calcium hydrogencarbonate has been given, and in fact all hydrogencarbonates are decomposed by heat liberating carbon dioxide.

Although some sodium hydrogencarbonate is used directly, most of it is converted to the more useful sodium carbonate. Full details of the production of sodium carbonate by the Solvay process will be studied later in the course. Here just some idea of its varied uses will be given. 35% of the sodium carbonate manufactured is used to make glass, 10% is used for making soap and another 10% in paper making. 17% is used in washing and bleaching textiles. Other uses include metal refining, making sodium hydroxide and other sodium compounds.

⁷ A lighted splint goes out when placed in a gas jar of carbon dioxide. Experiment 11.2, besides showing that carbon dioxide is denser than air, also shows that a candle will not burn in carbon dioxide. As well as preventing the burning of wood and paraffin wax, carbon dioxide also prevents the burning of paper, oil, petrol and similar substances. Experiment 11.3 shows that at least one substance does continue to burn in carbon dioxide – that is magnesium. The temperature of burning magnesium is sufficiently high to split the carbon dioxide and use the oxygen to form magnesium oxide, leaving behind a black deposit of carbon.

Magnesium + carbon dioxide $\longrightarrow$ magnesium oxide + carbon

$$2Mg + CO_2 \longrightarrow 2MgO + C$$
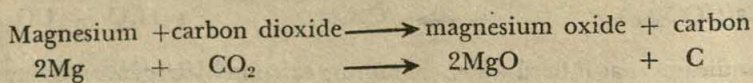
Carbon dioxide has been prepared for investigation by the action of an acid on a carbonate. In the course of other investigations it has been found that carbon dioxide can be formed directly by burning charcoal in oxygen, and it also results from heating some carbonates and bicarbonates. When the burning of a candle was studied in Chapter 4, carbon dioxide was the product trapped in the soda-lime; water being trapped by the calcium chloride. The burning of most fuels – wood, coal, charcoal, kerosene, petrol – results in the formation of carbon dioxide and water. Carbon dioxide is also a product of respiration. Although the normal percentage of carbon dioxide in air is given as 0.03%, in crowded towns and especially in rooms not sufficiently ventilated, the amount may increase ten-fold up to 0.3%. Another source of carbon dioxide is *fermentation*. In this process,

sugars are acted upon by yeast to give alcohol (ethanol) and carbon dioxide. For example,

Glucose $\longrightarrow$ alcohol + carbon dioxide

$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2 \uparrow$
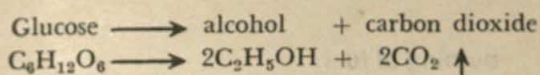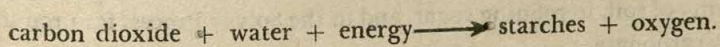
## 6. Uses of carbon dioxide

The carbon dioxide which is produced by fermentation is mainly used to make fizzy drinks. Joseph Priestley (one of the discoverers of oxygen) went to live in America at the end of his life. He told a friend in Philadelphia about the pleasant taste of a solution of carbon dioxide in water. This friend added fruit juices to the solution and started the industry which accounts for about 90% of carbon dioxide production.

A number of different types of fire extinguishers make use of carbon dioxide. The heavy gas forms a blanket over the fire excluding the air. In some fire extinguishers such as that illustrated in Fig. 11.3, the carbon dioxide is produced by the reaction between chemicals. In others, the carbon dioxide is present in the cylinder at high pressure and when released, carbon dioxide 'snow' cools the fire and blankets it to keep out the air. This type can be used safely on electrical equipment.

Solid carbon dioxide is used for refrigeration purposes, such as keeping ice cream and frozen foods cool when they are being moved. It has advantages over ice because it is much colder, it lasts longer and leaves no liquid residue because it sublimes and for this reason it is known as 'dry ice'.

In nuclear power stations, carbon dioxide is used to take away the heat from the core. The carbon dioxide becomes very hot and is then passed through tubes surrounded by water. The water is changed into steam which drives turbines connected to generators for the production of electricity.

Although man has his uses for carbon dioxide, they are only important in the quality of life and not for life itself. The one essential use of carbon dioxide is the natural use of it by plants. The naturally occurring substances of air, sea and land are simple inorganic compounds, which are no use to animals as food. Animals depend directly or indirectly on plants which are able to make food from simple substances. Of the processes which take place in plants, perhaps the most important is that of producing starches from the simple starting materials of carbon dioxide and water. For this process the light of the Sun is required and so it is known as *photosynthesis*. Sunlight has to be captured by the plant and this is mainly done by the green colouring matter in leaves — *chlorophyll*. Photosynthesis is a very complicated process but for convenience it can be represented as:

carbon dioxide + water + energy $\longrightarrow$ starches + oxygen.

Notice that as photosynthesis uses up carbon dioxide, it produces oxygen. This provides a check on the build-up of carbon dioxide in the atmosphere and replaces the oxygen used up in respiration and burning.

wire gauze

loose stopper

dilute sulphuric acid

sodium hydrogen carbonate solution

handle
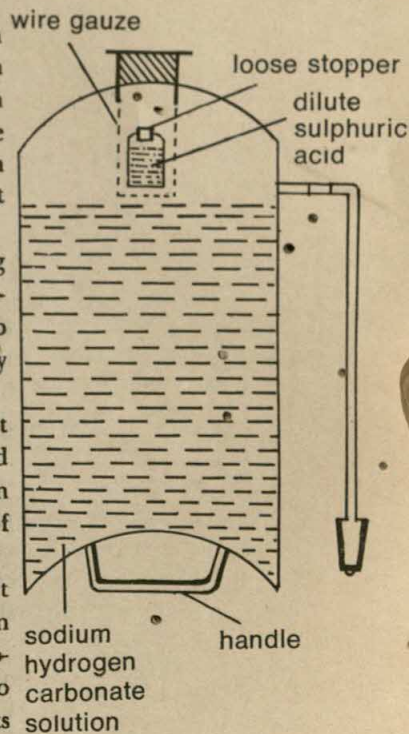
Fig. 11.3    **Principle of a Fire Extinguisher**

*To use, turn upside down so that the acid spills out and reacts with the sodium hydrogencarbonate*

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## The Carbon-Oxygen Cycle

burning of fuels

respiration

```
          ┌──────────────────────────────────┐
          │                                  ▼
    ┌──────────┐                      ┌──────────────┐
    │  oxygen  │                      │ carbon dioxide│
    │    +     │                      │      +        │
    │ starches │                      │    water      │
    └──────────┘                      └──────────────┘
          ▲                                  │
          └──────────────────────────────────┘
```

photosynthesis
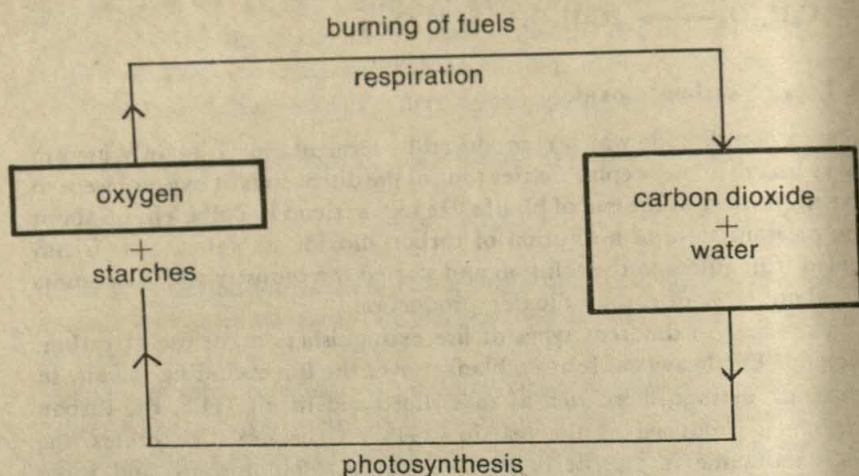
Fig. 11.4   **The Carbon-Oxygen Cycle**

This natural process which keeps going around and around is known as the carbon-oxygen cycle. In recent years the amount of carbon dioxide in the air has increased — in some places the normal figure now quoted is 0.04% rather than the previously accepted value of 0.03%. This increase is due to industrial development which besides producing more carbon dioxide, also leads to land on which plants grew being built upon. So there are less plants to take up the increased amount of carbon dioxide and restore life-giving oxygen to the air. This situation has already been discussed in an earlier chapter, where it was recommended that forests be carefully conserved and that in towns and cities trees and other plants should be part of the normal surroundings.

The importance of sodium carbonate has already been mentioned. The other important carbonate is calcium·carbonate. This occurs naturally as limestone, marble, chalk and Iceland Spar (calcite — a crystalline form). Limestone is used for making glass and in making iron and steel. Cement is made from limestone and clay. Although calcium carbonate cannot be decomposed by heat in the laboratory, the lime-kiln with temperatures around 1000°C brings about this change. Both the carbon dioxide and the calcium oxide produced have important uses. Bricks made from calcium oxide are used to line furnaces but most of it is treated with water (slaked) to give slaked lime (calcium hydroxide). Calcium hydroxide is used in the manufacture of sodium hydroxide, in water treatment, to counteract the acidity of soil, in refining sugar, and in the Solvay Process for producing sodium carbonate.

So, carbon dioxide and its related compounds have been studied in some detail. The important thing is to consider carbon dioxide, not just as a substance found in the chemistry laboratory but as something which is

necessary to life and which contributes to our welfare. Similarly the compounds studied have an important effect on our everyday life.

## Questions

1 How would you distinguish by chemical tests between air, oxygen and carbon dioxide?

2 Describe and explain what happens when carbon dioxide is passed into a solution of calcium hydroxide until no further change occurs.

3 State and explain what happens when: (a) a burning candle is plunged into a jar of carbon dioxide, (b) burning magnesium is plunged into a jar of carbon dioxide.

4 Of what does pure soda-water consist? What is its effect on (a) litmus (b) limewater?

5 How does calcium carbonate occur in nature? How would you obtain a sample of pure carbon from some calcium carbonate?

6 Since 'dry ice' costs several times as much as ordinary ice, how can it compete with ordinary ice?

7 Describe briefly two processes which tend to increase the amount of carbon dioxide in the air, and two which tend to decrease it.

8 Dilute acid is added to a rock called dolomite. The gas given off forms a white precipitate when bubbled through limewater. What can you say about the type of substance to which dolomite belongs?

9 You are given two white solids, sodium hydrogencarbonate and sodium carbonate. Describe one test by which you could distinguish between the two solids.

10 Explain the principle of the working of a 'fire extinguisher'.

11 Write a paragraph on the topic 'The importance of carbon dioxide in our lives'.

# Part 2
## FOR CLASS 8

# 12
# Water

A NUMBER of facts about water have been established during the course of studies so far. Its importance to life is equal to that of the air we breathe and no one would think of siting a city, town or village in a place unless adequate supplies of water were assured. The freezing point and boiling point of pure water are easily reproduced, and they are taken as fixed points on the Celsius (Centigrade) scale of temperature, 0°C and 100°C respectively. Air contains water vapour, which is the source for most of the freshwater which is in so much demand. To get pure water is not an easy task because water is such a good solvent, even dissolving minute quantities of glass, so that extra pure water has to be kept in platinum vessels. The presence of impurities lowers the freezing point and raises the boiling point. In passing, it has also been stated that water is a product of burning certain substances. Experiment 12.1 should be carried out in order to confirm this statement.
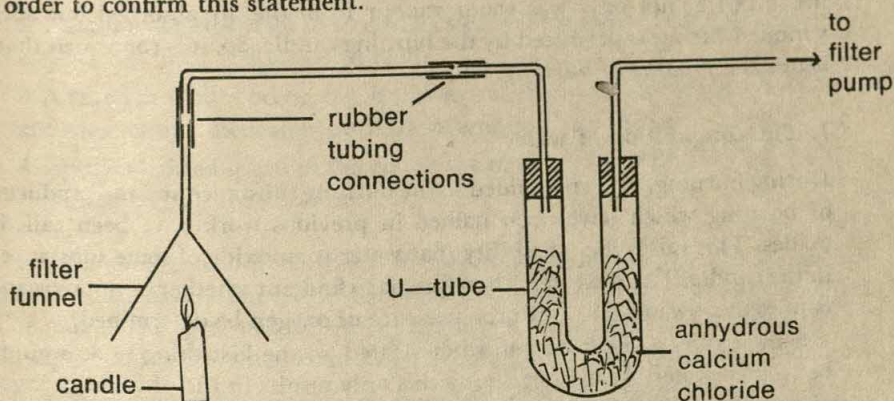


Fig. 12.1  **Water as a product of burning**

**EXPERIMENT 12.1   To show that water is a product of burning**

(a) Weigh the U-tube containing the anhydrous calcium chloride. Connect the apparatus as shown in Fig. 12.1 to a filter pump. Light the candle and turn on the filter pump. Allow the candle to burn for about ten minutes and then blow it out, disconnecting the pump at the same time. Do not turn the filter pump off. Re-weigh the U-tube.

(b) Repeat the experiment without lighting the candle, but allow the

same amount of air to pass through the U-tube by keeping the filter pump operating for the same length of time.

Before considering the results of Experiment 12.1, it must be remembered that anhydrous calcium chloride is a substance which will absorb water vapour. In Experiment 12.1(a), there is an increase in the weight of the U-tube. This can be accounted for by the anhydrous calcium chloride having absorbed water vapour. But where has this water vapour come from? One answer is 'from the air', another, 'from the burning candle', and, another, 'from both'. To select the correct answer from these alternatives, the second half of the experiment is carried out. Only one factor is changed — there is no candle burning. Thus this experiment serves as a good example of a scientific investigation. Where there is a possibility of several answers, each one is tested in turn by altering just one of the possible factors and keeping all the others the same. Consider possible results for Experiment 12.1(b). The U-tube could show a smaller increase in weight, the same increase or a larger one. Since a chemical reaction has been stopped, it is unlikely that there will be a larger increase in weight, but this possibility must be thought of, and only actual experimental results will show whether it can be discarded. This establishes another principle of scientific investigation — *there is no substitute for experimental facts*. If the U-tube shows the same increase in weight after each ten minute run, then this increase must be due to water vapour from the air only. It is to be expected, however, that the increase in weight in Experiment 12.1(b) will be less than that recorded in Experiment 12.1(a). This shows that in Experiment 12.1(a) not only was water vapour from the air absorbed but also vapour which was produced by the burning candle. So, it is confirmed that *water is a product of burning*.

## 1. The composition of water

During burning, oxygen is added to the burning substance and the products of burning which have been named in previous work have been called oxides. This raises the possibility that water is an oxide of some substance in the candle. The next step, therefore, is to find out whether or not oxygen is present in water. How can the presence of oxygen be determined?

Some oxides give off oxygen when heated, so the first thing to do would be to heat water. At the beginning this only results in the physical change of state from liquid to gas. As the temperature of steam is raised there is no detectable decomposition — water is a *stable* substance, it is not easily decomposed. As a matter of interest, it can be noted that less than 2% of it is decomposed when it is heated to 2000°C. So, if there is oxygen in water, it must be held very strongly to any other substances present. In order to get oxygen from water, it will therefore be necessary to find something which has a stronger attachment or *affinity* for oxygen than the other substance or substances in water. During the examination of the properties of carbon dioxide, there was one reaction which might give the necessary clue to the substance required now. Burning magnesium plunged into a gas jar of carbon dioxide removes the oxygen and leaves a black residue of carbon.

Carbon dioxide + magnesium ⟶ magnesium oxide + carbon.

$$CO_2 + 2Mg \longrightarrow 2MgO + C$$
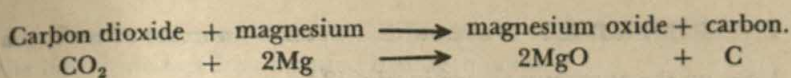
Because a temperature above 100°C is required for water to be in the gaseous state it is difficult to plunge burning magnesium into steam. The reaction between steam and magnesium is investigated in Experiment 12.2, using the apparatus shown in Fig. 12.2.
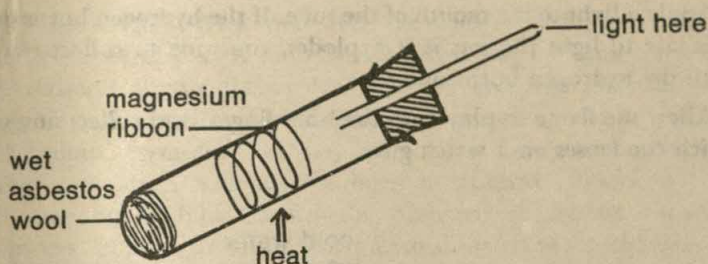


Fig. 12.2 **Magnesium heated in steam**

## EXPERIMENT 12.2

1. Put some wet asbestos wool into the bottom of a boiling tube. Take about 15 cm of magnesium ribbon cleaned with sandpaper, and after coiling it push it into the tube. Close the tube with a cork containing a short delivery tube.

2. Heat the asbestos wool so that some steam is produced. Then heat the magnesium until it appears to melt.

3. A reaction should occur, but if it does not then heat the asbestos wool and magnesium alternately until the magnesium does burn in the steam.

4. Apply a lighted splint to the end of the delivery tube to ignite the gas produced during the reaction.

It is reasonable to suppose that the white solid product of this reaction is magnesium oxide. The gas which burns is hydrogen which is an element. The name 'hydrogen' means 'water producer' and was given by Lavoisier. An equation for the reaction in this experiment can now be proposed:

Magnesium + water ⟶ magnesium oxide + hydrogen.
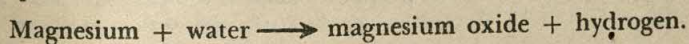
This reaction establishes the presence of oxygen and hydrogen in water, so water is a compound because it has been broken down into simpler substances. This method of investigating a substance by breaking it down into simpler substances is known as *analysis*.

Notice that no formula has been written yet for water. This is because where possible the results of analysis should be confirmed by *synthesis*, in which simple substances are put together to make a more complicated substance. In this case, it would appear that the elements hydrogen and oxygen make up the compound water. Since water is a product of burning, it is also possible that it is an oxide of hydrogen. Experiment 12.3 is designed to test this; hydrogen is burnt and the product then examined.

## EXPERIMENT 12.3  To show that water is an oxide of hydrogen

1. Set up the apparatus shown in Fig. 12.3.

2. Add dilute sulphuric acid to zinc to produce hydrogen. (Passing the gas through anhydrous calcium chloride ensures that it is dry). Before lighting the gas, a test tube of it should be collected by *upward delivery* (see Fig. 12.4).

3. Apply a light to the mouth of the tube. If the hydrogen burns quietly, it is safe to light the jet; if it explodes, continue to collect test tubes until the hydrogen burns quietly.

4. Allow the flame to play onto the 'cold finger' and collect any vapour which condenses on a watch glass.
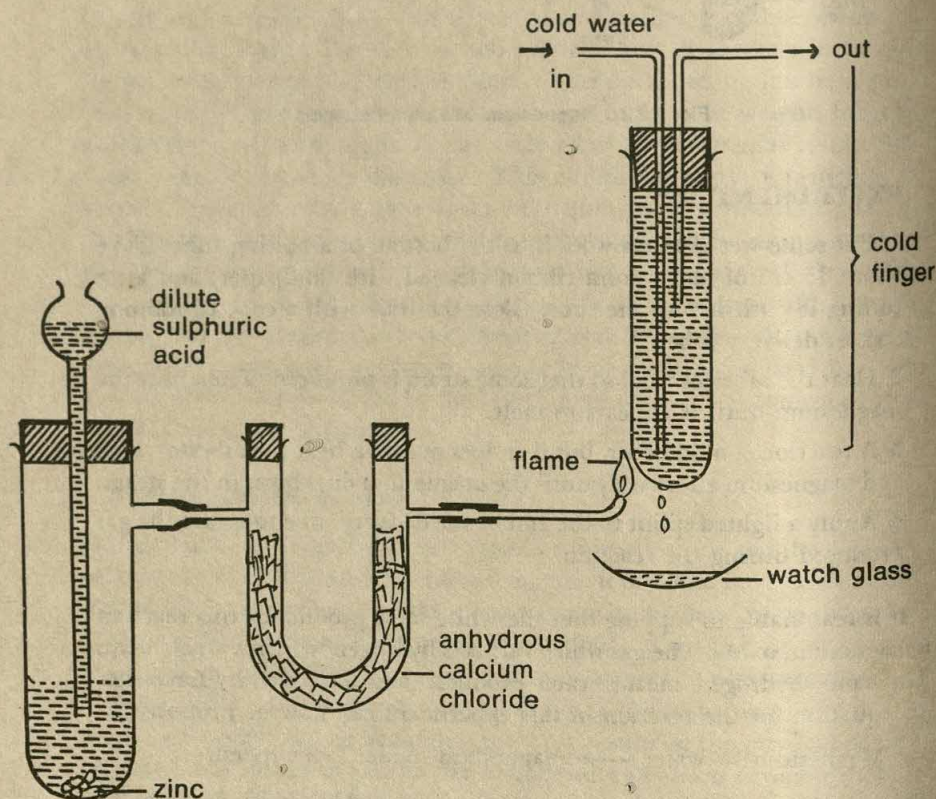


Fig. 12.3  **Synthesis of Water**

The final stage in this investigation is to examine the liquid formed when hydrogen burns. A white powder, anhydrous copper sulphate, can be used to show the presence of water. Add a drop of the product from Experiment 12.3 to some anhydrous copper sulphate; this will turn blue, which shows water to be present. The liquid certainly contains water, so that it is possible to say that water is formed when hydrogen burns. Before stating that water is the only product, the boiling point of the liquid should be checked.

The method is given in Chapter 2. The result of this check will show that the liquid produced by burning hydrogen is water.

$$\text{Hydrogen} + \text{oxygen} \longrightarrow \text{water.}$$
$$2H_2 + O_2 \longrightarrow 2H_2O$$
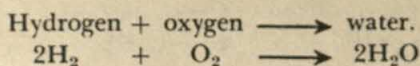
## 2. The formula of water

Why write $H_2O$? Why not HO, or $HO_2$, or $H_3O$ or any other combination of atoms? It must be admitted that for some 50 years or so after Dalton's atomic theory HO was the accepted formula. Why the change? These questions have been raised in order to make you begin to think about formulas. So far, you have been told the formulas of the compounds which have been mentioned. Reactions involving these compounds have shown the presence of certain elements and this process of analysis could continue to show all of the elements present as with water. This is known as *qualitative analysis* which means finding out which substances are present. To find out how much of each substance is present it is necessary to carry out *quantitative analysis*. At this stage all that can be said is that the quantitative analysis of water, including the measure of the volumes of hydrogen and oxygen which combine together, shows that the water molecule should be given the formula $H_2O$. In Chapter 17, information will be given to enable you to write formulas correctly. Some of the results of quantitative analysis will also be introduced in Chapter 18 and formulas worked out from these. The point to be made at this stage is that 'formulas do not just happen'; they are based upon experimental results.

## 3. The reaction of water with metals

The reactions of other metals with water help to confirm that water is a compound of hydrogen and oxygen. These reactions are also of interest in understanding the chemistry of metals and so they are studied in the following experiments.

### EXPERIMENT 12.4

Care: The experiments with sodium and potassium should be watched from a distance of 2 metres or more in case pieces of molten metal jump out of the trough.

(a) Take a small piece of freshly-cut sodium (about the size of a rice grain) and drop it on to the surface of cold water in a trough. What happens to the sodium? Add a drop of Universal indicator to the water in the trough. Is the solution acidic or alkaline?

(Also carry out this experiment with potassium, if available).

(b) With fresh water in the trough, float a filter paper on it and then place another small piece of freshly-cut sodium on the moist filter paper. What happens this time?

(c) Put a small piece of clean calcium into a trough of water. What happens to the calcium? Invert a test tube full of water over the calcium
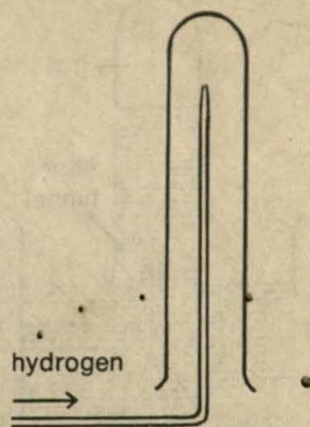


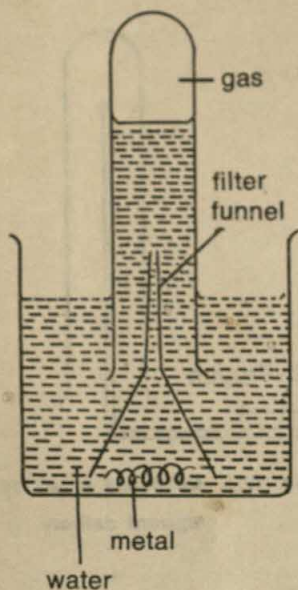Fig. 12.4  **Collecting a gas by upward delivery**

hydrogen

gas

filter
funnel

metal

water

Fig. 12.5  **Action of Water
on Metals**

and collect the gas given off. Test the gas with a lighted splint. Put a
few drops of Universal indicator into the water and note the result.

### EXPERIMENT 12.5

With the apparatus shown in Fig. 12.5, use the following metals:
magnesium, aluminium, zinc, iron, lead and copper. Set up six sets of
apparatus at the same time and leave them to stand with the metal in
the water for a week. Compare the amounts of gas, if any, collected in
the test tubes. Test the gas with a lighted splint. If there is not enough
gas to test, can you say what you expect it to be?

In Experiment 12.5, only magnesium will give an appreciable quantity
of hydrogen. In Experiment 12.2, steam was passed over heated magnesium,
so that the effect of magnesium on two gases, carbon dioxide and steam,
could be compared. From Experiment 12.5, it is apparent that, in any
case, for any reasonable rate of reaction to occur, steam is necessary.
Experiment 12.6 is designed to test the effect of steam on some of the
other metals which do not react with cold water.

### EXPERIMENT 12.6

1. Use the apparatus shown in Fig. 12.6 with aluminium powder, zinc
dust and iron filings in turn.

2. Heat the metal gently and then move the flame backwards and for-
wards, boiling the water and keeping the metal hot. Collect any gas
produced over water and test to see if it is hydrogen.



finely divided
metal

gas

wet
asbestos     heat
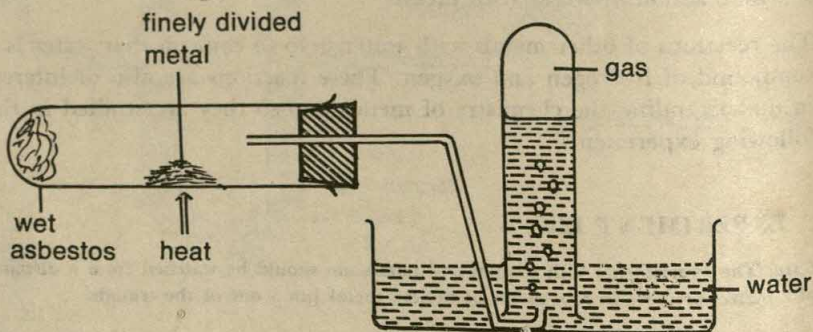
water

Fig. 12.6  **Action of Steam on Metals**

Following Experiments 12.4, 12.5 and 12.6, it is possible to say that some
metals react with water and others with steam, producing hydrogen. Know-
ing that water contains hydrogen and oxygen, the other product can be
expected to be an oxide of the metal as already observed with magnesium.
However, in the case of sodium and calcium, the oxide reacts with more
water so that a hydroxide is formed which is soluble and which gives an
alkaline solution. Equations can now be written for the reactions which
have been investigated.

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(i) Sodium       + water $\longrightarrow$ sodium hydroxide    + hydrogen.
    2Na          + 2H$_2$O $\longrightarrow$     2NaOH           + H$_2$ ↑

(ii) Calcium     + water $\longrightarrow$ calcium hydroxide   + hydrogen.
     Ca          + 2H$_2$O $\longrightarrow$     Ca(OH)$_2$     + H$_2$ ↑

(iii) Magnesium + water $\longrightarrow$ magnesium oxide      + hydrogen.
      Mg         + H$_2$O $\longrightarrow$      MgO            + H$_2$ ↑

(iv) Zinc        + water $\longrightarrow$ zinc oxide          + hydrogen.
     Zn          + H$_2$O $\longrightarrow$      ZnO            + H$_2$ ↑

(v) Iron         + water $\longrightarrow$ magnetic oxide of iron + hydrogen.
    3Fe          + 4H$_2$O $\longrightarrow$     Fe$_3$O$_4$    +     4H$_2$ ↑
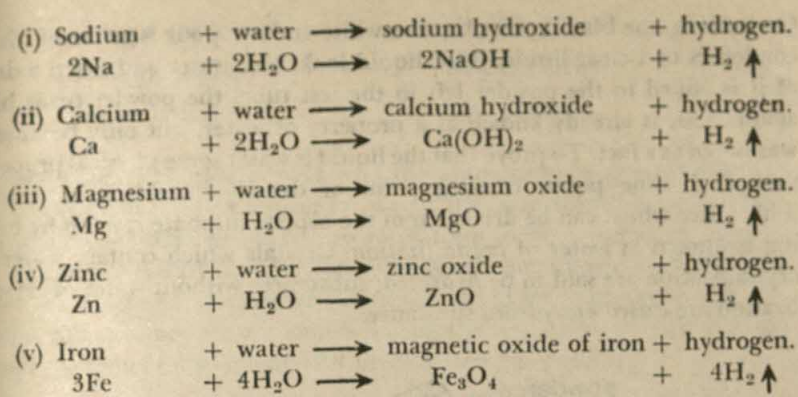
These reactions also show that the metals have differing activities when brought into contact with water. Potassium and sodium attack cold water vigorously, with calcium and magnesium the reaction is less vigorous. Aluminium, zinc and iron have to be heated in steam before a reaction takes place and some metals like copper just do not react. Placing these metals in order of their activity with water, the order is:

Potassium        most reactive
Sodium
Calcium
Magnesium
Aluminium                        Decreasing activity
Zinc
Iron
Lead
Copper           no reaction
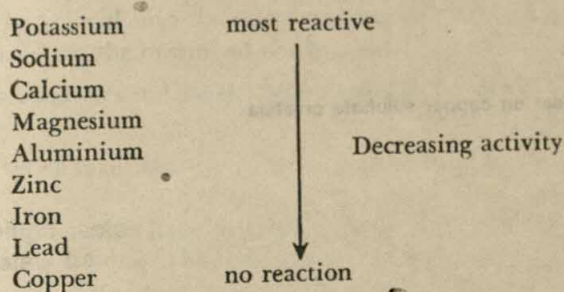
Not only does this order apply to the reactions of the metals with water, but it is found that other features of the chemistry of metals follow the same pattern — for example, their reactions with oxygen and their reactions with acids. This makes it possible to summarize a lot of chemistry within one system of classification which is known as 'The Metal Activity Series'. Details of this series will be filled in throughout the course.

## 4. Water of crystallization; hydrated and anhydrous substances

At the end of Experiment 12.3, a white powder called anhydrous copper sulphate was used to indicate the presence of water. This white powder turns blue when it comes into contact with water. Normally, if you asked for copper sulphate you would be given a dry, blue crystalline solid. The blue colour is like that obtained when water is added to anhydrous copper sulphate and so we can suppose that there is some connection between water and the blue colour.

## EXPERIMENT 12.7

Crush some copper sulphate crystals and put them into a test tube. Connect the test tube with the rest of the apparatus as shown in Fig. 12.7. Gently heat the crystals and see what happens.

On heating, the blue crystals become white and a vapour is given off which condenses to a clear liquid. This liquid looks like water and when a drop of it is added to the powder left in the test tube, the powder turns blue again. This is already known as a property of water, but only because it was stated as a fact. To prove that the liquid is water some physical property such as boiling point, freezing point or density should be measured. This water which can be driven from the copper sulphate crystals by heating is known as *water of crystallization*. Crystals which contain water of crystallization are said to be *hydrated*; substances without water of crystallization are called *anhydrous* substances.
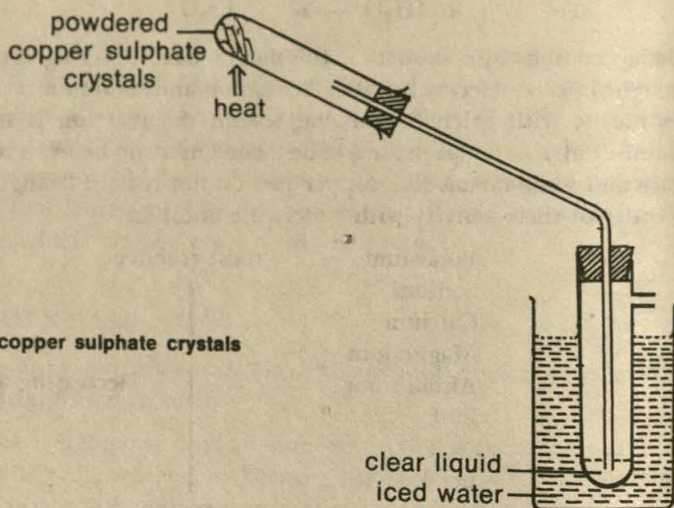


Fig. 12.7 **Action of heat on copper sulphate crystals**

Hydrated copper sulphate $\rightleftharpoons$ anhydrous copper sulphate + water

$$CuSO_4.5H_2O \rightleftharpoons CuSO_4 + 5H_2O$$
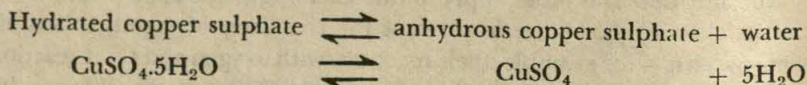
The symbol $\rightleftharpoons$ is used to show that the hydrated copper sulphate will give anhydrous copper sulphate and water, but that this can be *reversed* by adding water to copper sulphate. The $5H_2O$ represents five molecules of water of crystallization and these are a definite part of the hydrated copper sulphate. This leads to the following definition of water of crystallization:

*Water of crystallization is a fixed proportion of water included within the structure of a crystalline substance.*

Not all crystals contain water of crystallization. For example, sodium chloride and sodium nitrate do not. Also, it should be noted that not all substances having water of crystallization can be dehydrated (made anhydrous) by heating.

Some hydrates:

| Name | Formula |
|---|---|
| Copper sulphate | $CuSO_4.5H_2O$ |
| Magnesium sulphate | $MgSO_4.7H_2O$ |

| Sodium carbonate | $Na_2CO_3.10H_2O$ |
| Sodium sulphate | $Na_2SO_4.10H_2O$ |
| Cobalt chloride | $CoCl_2.6H_2O$ |
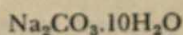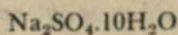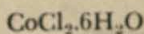
Hydrated cobalt chloride is pink and the anhydrous compound is blue. This fact is often used in testing for water, the blue anhydrous substance turning pink as it changes to the hydrated form in the presence of water.

In Experiments 12.1 and 12.3 anhydrous calcium chloride was used to remove water vapour from other gases. Anhydrous calcium chloride is one example of a number of compounds having the similar property of taking up water vapour. Experiment 12.8 investigates this property.

## EXPERIMENT 12.8

1. Place small quantities of the following substances on separate watch glasses: sodium hydroxide, anhydrous calcium chloride, sodium nitrate, iron (III) chloride (ferric chloride).

2. Also, take two beakers and put ethanol (alcohol) into one and concentrated sulphuric acid into the other to a depth of about 2 cm. Mark the liquid level on the outside of the beakers.

3. Leave all the watch glasses and beakers with their contents in the open air for several days.

Note any changes which take place.

In Experiment 12.8, the solids have absorbed water vapour from the air and formed saturated solutions. They are known as *deliquescent* substances and the property – *the absorbing of water vapour from the air forming a saturated solution* – is known as *deliquescence*. The ethanol and concentrated sulphuric acid have also absorbed water vapour, but no change of state has taken place. Some solids such as copper oxide and calcium oxides will also absorb water vapour from the atmosphere without change of state. These substances are known as *hygroscopic* substances.

*A hygroscopic substance is one which absorbs water vapour from the air without change of state.*

Experiment 12.9 illustrates what might be considered the reverse situation to the absorption of water vapour by deliquescent and hygroscopic substances.

## EXPERIMENT 12.9

Expose crystals of sodium carbonate and sodium sulphate on separate watch glasses to the open air. Note any changes which take place after several days.

The crystals are seen to become covered with a white powder and then crumble completely into a mass of powder. The hydrates have given up part or all of their water of crystallization. This is known as *efflorescence* –

the giving up of water of crystallization to the atmosphere — and the substances are said to be *efflorescent*.

## 5. Hard and soft water

The last part of this chapter deals with one of the effects which results from the good solvent properties of water. Of everyday importance is the use of soap for personal cleanliness and for the washing of dishes and clothes. Sometimes, though, the soap is not as effective as it could be and instead of getting a *lather* easily (that is, lots of tiny soap bubbles on the surface of the water) an unpleasant *scum* is formed. This may not be so noticeable as the fact that in different places throughout the country more soap or less soap is required to make a good lather. If there is difficulty in forming a lather then the water is said to be *hard*.

*Hard water is water which will not readily form a lather with soap.* Where a lather forms readily, the water is *soft*.

The softest water is distilled water, and it is the presence of various solutes in the water which contribute to its hardness. These substances react with the soap to form insoluble compounds which make up the scum. It is not until these reactions have taken place that a lather can form, so hard water is wasteful of soap. Experiment 12.10 helps to identify substances responsible for the hardness of water.

### EXPERIMENT 12.10

1. Make a soap solution by dissolving about 1 g of soap flakes in a mixture of 100 cm³ of distilled water and 100 cm³ of industrial spirits.

2. Dissolve, in about 10 cm³ of distilled water in different test tubes, about 0.1g of sodium chloride, calcium chloride, magnesium chloride, potassium nitrate, sodium sulphate and magnesium sulphate.

3. Add 1 cm³ of soap solution to each test tube and shake. Compare the lathers formed and divide the solutes into those which prevent the formation of a good lather and those which do not.

Compounds of calcium and magnesium are seen to be responsible for hard water. These have to be soluble and get into the water as it flows over or through rocks containing these compounds. The most common substances causing hardness are calcium sulphate, which is present because many rocks and soils contain gypsum ($CaSO_4.2H_2O$), and calcium hydrogen-carbonate, which is present due to the action of rainwater containing dissolved carbon dioxide running through rocks and soils in which there is limestone or chalk.

Calcium carbonate + water + carbon dioxide $\longrightarrow$ calcium hydrogencarbonate.
(limestone)          (rainwater)

$$CaCO_3 \quad + H_2O + \quad CO_2 \quad \longrightarrow \quad Ca(HCO_3)_2$$
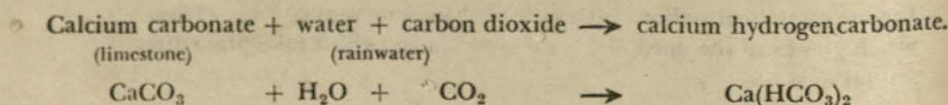
From the earlier study of carbon dioxide and carbonates, it is known that when a solution containing calcium hydrogencarbonate is boiled, a precipitate of calcium carbonate is formed. This removes the soluble

calcium compound and the water becomes soft. This hardness which can be removed by boiling is called *temporary hardness*. The other soluble calcium compounds give rise to *permanent hardness* which cannot be removed by boiling.

## 6. Disadvantages of hard water

Hard water is a disadvantage because its presence involves the wasteful use of soap and also because it spoils the finish of fabrics, causes off-shades in dyeing and prevents successful tanning of leather. If temporary hardness is present in water that has to be heated it is an added nuisance. The precipitation of calcium carbonate, by the reaction,

Calcium hydrogencarbonate $\longrightarrow$ calcium carbonate + water + carbon dioxide.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_2$$
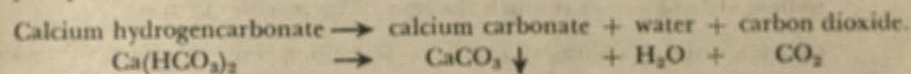
gives 'fur' in kettles and 'scale' in boilers and pipes. So the heat has to pass through layers of calcium carbonate before reaching the water being heated. The scale in pipes may lead to blockages followed by explosions.

## 7. Methods of removing hardness

In view of these disadvantages it is not surprising that means of removing the hardness, that is, of softening, have been developed. Distillation of water will result in water from which all the dissolved solids have been removed, but this is an expensive process. Likewise, temporary hardness could be removed by boiling and filtering, but this also is too expensive to use on a large scale.

Temporary hardness alone can be removed by using Clark's Process. This involves the addition of a carefully calculated amount of calcium hydroxide so that the calcium is removed as the insoluble carbonate.

Calcium hydrogencarbonate + calcium hydroxide $\longrightarrow$ calcium carbonate + water

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$
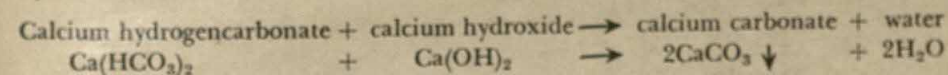
Calcium hydroxide is itself slightly soluble in water, so what would happen if too much of it were added?

Other methods of softening can be applied to both types of hardness. Washing soda is the common name given to hydrated sodium carbonate $(Na_2CO_3.10H_2O)$. When this is added to water containing any soluble calcium compound, the calcium is removed as insoluble calcium carbonate. Although a sodium compound remains in solution, the water is softened because this compound does not react with soap.

Calcium sulphate + sodium carbonate $\longrightarrow$ calcium carbonate  sodium sulphate.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$
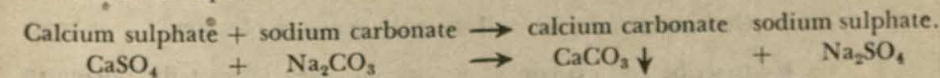
In the 'Calgon' process, sodium metaphosphate is added to the water and this traps the calcium so that it cannot react with the soap.

A widely used method of water softening involves the use of *ion-exchange* materials. A full appreciation of this method is not possible at present because the word ion needs an explanation which only comes later in our study of chemistry. Briefly, the process involves the exchange of calcium

hard water (temporary or permanent hardness)

ion-exchange resin

soft water
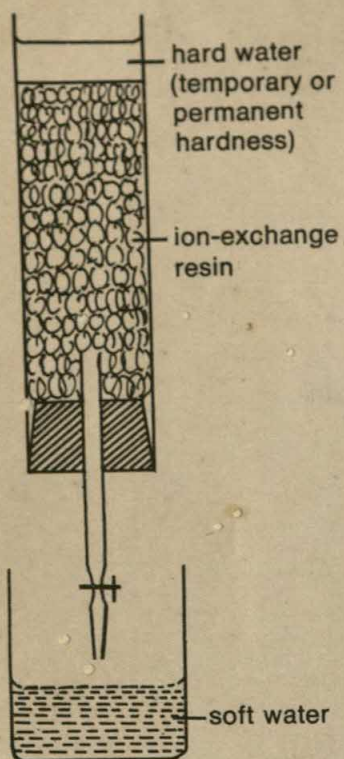
Fig. 12.8  Model Water Softener

in the hard water for sodium which is in the ion-exchange material called a *resin*. This exchange softens the water because sodium compounds do not react with soap. Fig. 12.8 shows a model of a water softener using an ion-exchange resin.

Calcium sulphate + sodium resin ⟶ calcium resin + sodium sulphate.
$$CaSO_4 \ + \ Na_2(resin) \ \longrightarrow \ Ca(resin) \ + \ Na_2SO_4$$
in - as  hard  water                       out — unreactive with soap
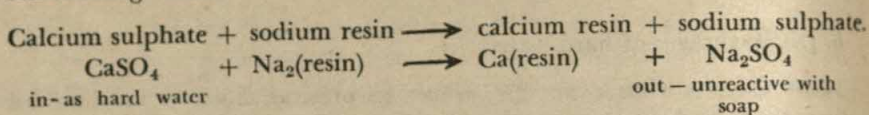
After a time there is no more sodium to replace the calcium, but instead of throwing the resin away it can be turned back to sodium resin. This is called *regenerating* and is done by pouring a concentrated solution of sodium chloride down through the resin. The reaction then is:

Calcium resin + sodium chloride ⟶ sodium resin + calcium chloride.
$$Ca(resin) \ + \ 2NaCl \ \longrightarrow \ Na_2(resin) \ + \ CaCl_2$$
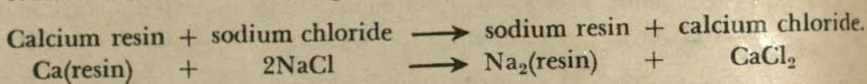
Any remaining sodium chloride and calcium chloride are washed out with water and the softener is ready for use again.

## 8. Advantages of hard water

Hard water is softened because there are disadvantages associated with its use, but there are also some advantages. For bone and teeth formation calcium is an essential item of diet and so the best drinking water contains 50 − 120 parts per million of calcium compounds. These incidentally give a better taste to the drinking water. In the past when lead pipes were common, soft water would dissolve some of the lead which is a poison, whereas hard water coated the inside of the pipes with insoluble lead sulphate and did not carry any poisonous dissolved lead. Of interest to some is the fact that hard water is good for making beer.

## Questions

1  Devise an experiment to show that water is a product of the burning of the gas used in Bunsen burners.

2  What is meant by saying that water is a stable substance?

3  Give two reasons for supposing that water is a compound.

4  Explain the terms *analysis* and *synthesis*.

5  Give two tests which will show the presence of water.

6  Describe and explain what happens when (a) metallic calcium is dropped into water (b) magnesium ribbon is heated in steam.

7  What is water of crystallization? Give the formulas for two substances containing water of crystallization.

8  What is the effect of leaving anhydrous calcium chloride exposed to the air?

9   When 30g of hydrated sodium carbonate crystals are left in dry air for some time a loss in weight of about 17g occurs. How do you account for this?

10  What is hard water? Explain the difference between (a) temporary, and (b) permanent hardness in water.

11  Name one substance causing temporary hardness of water and explain how it gets into the water.

12  Give two disadvantages of hard water and describe two ways in which all the hardness in water can be removed.

13  Explain why (a) boiling, (b) addition of calcium hydroxide, removes temporary hardness of water but not permanent hardness. Give the appropriate equations.

14  Outline how you would compare the hardness of samples of tap water and rain water.

# 13
# Hydrogen

THE analysis of water described in the last chapter, introduced the inflammable gas named hydrogen whose name means 'water producer'. It was seen that hydrogen could be liberated from water (or steam) by the action of metals. Despite the abundance of water, it was not until just over 300 years ago that the existence of hydrogen was suspected when Robert Boyle saw bubbles of a gas form after iron was placed in sulphuric acid. About 100 years later, Henry Cavendish used the action of dilute sulphuric acid on metals to prepare hydrogen in quantity so that he could examine its properties. It was Cavendish who discovered that hydrogen burns, and in 1781 he proved that water is the only product of the burning of hydrogen in air (see Experiment 12.3).

## 1. Laboratory preparation of hydrogen

The action of metals on water is either too violent so that hydrogen cannot be collected, or it is too slow if a reasonably large quantity of hydrogen is required. So, in the laboratory, it is usual to use Cavendish's method. Experiment 13.1 investigates the reaction between metals and an acid.

### EXPERIMENT 13.1  Reaction of hydrochloric acid with metals

1. Put a small piece of magnesium into a test tube and pour in some dilute hydrochloric acid to a depth of 2 or 3 cm. What do you see?

2. Put a lighted splint near the mouth of the tube. What happens?

3. Repeat the experiment using copper turnings, zinc, lead, iron filings and aluminium. If there is no reaction with the cold dilute acid, warm the test tube gently.

Set out your observations in a table as shown.

| Metal | Heat needed? | Hydrogen formed? | How vigorously? |
|-------|--------------|------------------|-----------------|
| Magnesium | | | |
| Copper | | | |
| Zinc | | | |
| Lead | | | |
| Iron | | | |
| Aluminium | | | |

The results of Experiment 13.1 can be used to place the metals in order of their activity with an acid. Compare the order obtained with that given in Chapter 12 after Experiments 12.4, 12.5 and 12.6. The reactions of the metals with acids is another illustration of the convenience of classifying metals in the activity series. The results of Experiment 13.1 also make it possible to select the most suitable metal for use in the laboratory preparation of hydrogen. The choice is quickly narrowed to magnesium or zinc since heat is required to produce any reasonable amount of hydrogen in other cases. Zinc is chosen because the stream of gas is steady, whereas magnesium produces hydrogen too rapidly for it to be collected easily. The equation for the reaction, described in Experiment 13.2, is:

$$\text{Zinc} + \text{hydrochloric acid} \longrightarrow \text{zinc chloride} + \text{hydrogen.}$$
$$\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2 \uparrow$$
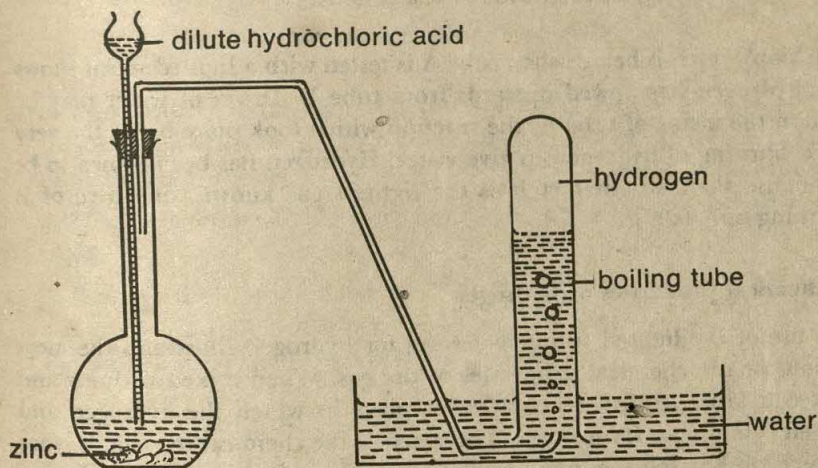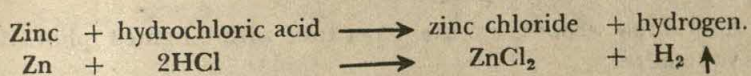


Fig. 13.1 **Laboratory Preparation of Hydrogen**

**EXPERIMENT 13.2 Reaction of hydrochloric acid with zinc**

1. Set up the apparatus as shown in Fig. 13.1. Before pouring the dilute hydrochloric acid onto the zinc, add a few drops of copper sulphate solution which will help to speed up the reaction if very pure zinc is used. Collect the hydrogen over water in boiling tubes, closing the mouths of the tubes with rubber bungs before lifting them out of the water.

2. Discard the first two or three tubes full since they will contain displaced air.

3. Before disconnecting the apparatus, dip the delivery tube into a solution of detergent (e.g. detergent mixed with an equal volume of water).

4. Note the formation of bubbles, and what happens to them as they break away. When a bubble of hydrogen is clear of the apparatus, touch it with the flame of a lighted splint. What happens?

## 2. Physical properties of hydrogen

Observations during the course of Experiment 13.2, reveal some of the physical properties of hydrogen. It is a colourless gas which is insoluble in water. Pure hydrogen does not have any smell. The rapid upward movement of the soap bubbles shows that hydrogen is less dense than air. Experiment 13.3 is another way of showing the same thing.
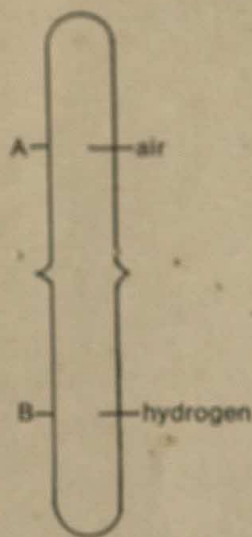
Fig. 13.2  Testing the Density of Hydrogen

**EXPERIMENT 13.3**  To show that hydrogen is less dense than air

1. Test tube A is a dry test tube containing air. Place it over a tube of hydrogen as shown in Fig. 13.2.

2. After a few seconds, test the upper tube with a lighted splint. What do you notice?

3. Look carefully at the inside of test tube A.

The 'pop' which is heard when tube A is tested with a lighted splint shows that hydrogen has flowed upwards from tube B. Drops of water may be seen on the inside of tube A, the reaction which took place being the very rapid burning of hydrogen to give water. Hydrogen has been shown to be less dense than air, in fact it is the lightest gas known, one litre of it weighing only 0.09 g.

## 3. Chemical properties of hydrogen

The use of the lighted splint in testing for hydrogen illustrates the most obvious of the chemical properties of the gas. When mixed with air and ignited a fast chemical reaction takes place in which the hydrogen and oxygen combine to form water. The speed of the chemical reaction is what is noted on hearing the 'pop'. Explosions such as those between hydrogen and oxygen are examples of fast chemical reactions. If a test tube full of pure hydrogen is taken and a lighted splint applied to its mouth, the hydrogen burns quietly with a pale blue flame.

Hydrogen + oxygen $\longrightarrow$ water.
$$2H_2 \ + \ O_2 \ \longrightarrow \ 2H_2O$$
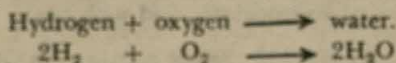
Hydrogen combines vigorously with oxygen to form water which is a stable compound. However, in Chapter 12 it was shown that some metals have an even stronger attraction for oxygen than hydrogen does, so the reaction

Metal + water $\longrightarrow$ metal oxide + hydrogen
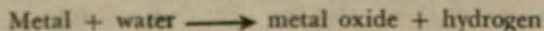
takes place. In the competition for oxygen, the metal wins. This leads to the question — in the competition for oxygen are there any metals which might lose to hydrogen? Metals which are unable to take the oxygen from water have already been encountered, and it is reasonable to suppose that hydrogen could be used to take the oxygen from the oxides of these metals, i.e.

metal oxide + hydrogen $\longrightarrow$ metal + water.
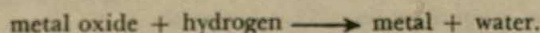
**EXPERIMENT 13.4** Reaction of hydrogen with metal oxides

Carry out this experiment with (a) copper oxide, (b) lead oxide.

1. Put some copper oxide into a porcelain boat and put this boat into a hard glass tube as shown in Fig. 13.3.
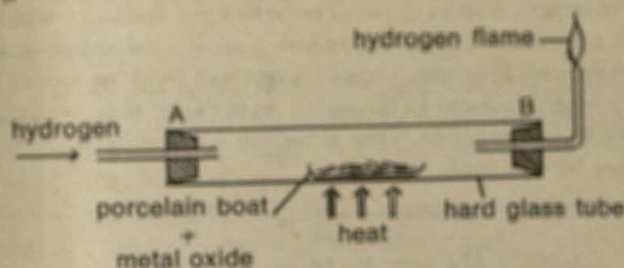


Fig. 13.3 **Reduction of Metal Oxide by Hydrogen**

2. Pass hydrogen through the tube and after about thirty seconds (ensuring that there is no air mixed with the hydrogen) light the stream of hydrogen at the jet.

3. Heat the copper oxide gently and observe any changes which take place.

4. Remove the Bunsen flame and let the tube cool with the hydrogen still passing through it. When the tube is cool, examine the contents of the boat. Repeat the experiment using lead oxide.

In this experiment beads of lead are seen clearly, but it is more difficult to identify the reddish-brown powder left behind, after heating copper oxide in hydrogen, with copper. That this powder is a metal can be confirmed by including it in an electric circuit with a bulb and battery. If the temperature used is not too high, the condensation of water vapour should be observed at B. These results can be expressed in the following equations:

Copper oxide + hydrogen $\longrightarrow$ copper + water.
$\quad$ CuO $\quad$ + $\quad$ H$_2$ $\quad$ $\longrightarrow$ $\quad$ Cu $\quad$ + H$_2$O

Lead oxide + hydrogen $\longrightarrow$ lead + water.*
$\quad$ PbO $\quad$ + $\quad$ H$_2$ $\quad$ $\longrightarrow$ $\quad$ Pb $\quad$ + H$_2$O
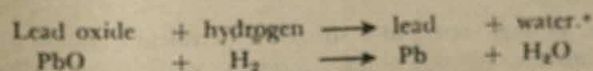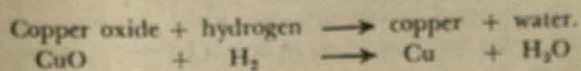
One other reaction needs to be mentioned here. As written in Chapter 12, the reaction between iron and steam is

Iron + water $\longrightarrow$ magnetic oxide of iron + hydrogen
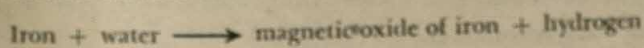
and this indicates that iron can remove oxygen from water. This is not the whole truth because when hydrogen is passed over heated magnetic oxide of iron, water is formed and iron is left behind. So, the change is reversible, the direction in which it goes depending on the conditions, and it is better represented as;

Iron + water $\rightleftharpoons$ magnetic oxide of iron + hydrogen.

$3Fe + 4H_2O \rightleftharpoons \qquad Fe_3O_4 \qquad + 4H_2$
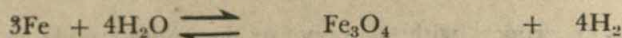
These reactions in which oxygen has been removed from compounds are clearly the reverse of the oxidation processes mentioned earlier. The removal of oxygen is an example of *reduction* and hydrogen which brings about the reduction is known as a *reducing agent*. Consider the reaction of copper oxide with hydrogen. Oxygen is removed from the copper oxide so this compound is reduced to the metal. At the same time, hydrogen takes up oxygen so it is oxidized. Thus reduction is accompanied here, and in other cases, by oxidation.

$$\begin{array}{c} \overset{\displaystyle \ulcorner\quad\text{reduced}\quad\urcorner}{}\;\;\downarrow \\ CuO + H_2 \longrightarrow Cu + H_2O \\ \underset{\displaystyle\llcorner\quad\text{oxidized}\quad\lrcorner\;\uparrow}{} \end{array}$$
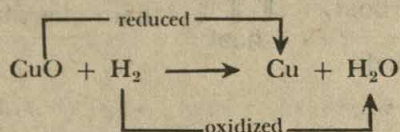
## 4. Industrial preparation of hydrogen

The uses of hydrogen are of increasing importance so that it now has to be manufactured in very large quantities. The most obvious source of hydrogen is the vast amount of water covering the Earth's surface, and it is made use of in the Bosch Process. Steam is passed over white hot coke (a form of nearly pure carbon); the gas issuing from the process being known as water gas.

Coke + steam $\longrightarrow$ carbon monoxide + hydrogen

$\quad C \quad + H_2O \longrightarrow \qquad CO \qquad + \quad H_2$
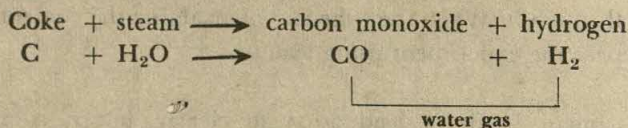
$$\underset{\text{water gas}}{\underbrace{\qquad\qquad\qquad}}$$

Water gas is mixed with more steam and passed over a catalyst at about 500°C. This results in a mixture of carbon dioxide and hydrogen. The carbon dioxide is removed by dissolving it in water under pressure.

$$CO + H_2O \longrightarrow H_2 + CO_2$$
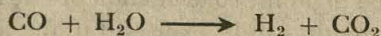
This reaction is known as the 'water-gas shift' reaction, and it is an important stage in the more up-to-date processes which are replacing the Bosch Process. India's big fertilizer plant in Sindri however continues to use the Bosch Process.

Besides water, another source of hydrogen is petroleum. Almost all of petroleum is a mixture of compounds containing carbon and hydrogen only, known as hydrocarbons. When hydrocarbons are mixed with steam and passed over a nickel-chromium catalyst at 750°C, carbon monoxide and hydrogen are formed.

Examples of some reactions are:

Methane + steam $\longrightarrow$ carbon monoxide + hydrogen.

$\quad CH_4 \quad + H_2O \longrightarrow \qquad CO \qquad + \quad 3H_2$

Heptane + steam $\longrightarrow$ carbon monoxide + hydrogen.

$\quad C_7H_{16} \quad + 7H_2O \longrightarrow \qquad 7CO \qquad + \quad 15H_2$
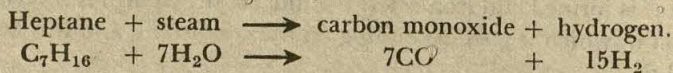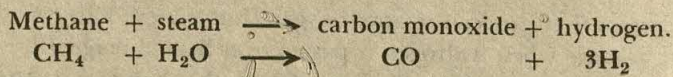
The carbon monoxide is removed through the water-gas shift reaction already given. Methane is the main constituent of natural gas and heptane is taken as an example of a gas which can be obtained from an oil refinery. Hydrogen is also available as a by-product from a number of processes which will be discussed at a later stage.

## 5. Uses of hydrogen

Most of the hydrogen which is manufactured is combined with nitrogen to form the gas ammonia ($NH_3$). It has been mentioned that ammonia is a starting point for making fertilizers, so the significance of this information about hydrogen becomes apparent.

Hydrogen is also used for making vanaspati and margarine from vegetable oils. Oil is squeezed out of ground-nuts, mustard seeds, cottonseeds, sunflower seeds or other seeds. Hydrogen is bubbled through the hot oil which contains finely divided nickel as catalyst, the product being a substance which is a solid fat at room temperature.

On account of its low density hydrogen is used to fill balloons. These are not just the toys of children but the balloons used by scientists to study the weather. Small ones are used to indicate wind speed and direction, and larger ones carry instruments such as barometers and thermometers to high altitudes. The disadvantage of hydrogen is its inflammability and this has resulted in the past in some terrible disasters involving airships. In 1930 an airship, the R101, hit a hillside in France on its maiden voyage to India and in the fire and explosion which followed forty-eight people were killed. Most countries lost interest in the possibility of using airships for air travel as a result. Germany persevered with the airship, but in 1937, their giant airship Hindenburg exploded at the end of a journey from Germany to America.

When hydrogen burns a large amount of heat is released, and it is used as a fuel for this reason. Most commonly this is as a constituent of coal gas which is supplied for cooking purposes in a number of Indian cities. Coal gas may contain up to 55% of hydrogen. Saturn V rockets have already been mentioned when oxygen was discussed; they are powered by the combustion of hydrogen. When oxygen and hydrogen are supplied separately at a blow pipe jet (see Fig. 13.4), an intensely hot blue flame with a temperature of approximately 2800°C is produced.
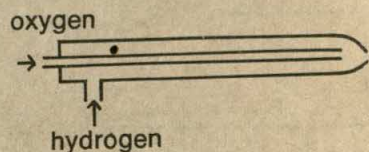


Fig. 13.4 **The oxy-hydrogen flame**

## Questions

1  Why is the reaction of metals with water not normally used as a means of preparing hydrogen?

2  Metals react with dilute hydrochloric acid liberating hydrogen. Which metal would you use in the laboratory preparation of hydrogen? Give reasons for your choice.

3  What are the physical properties of hydrogen?

4   With what gas does hydrogen combine when it burns in air? Name the product. Why is this product not visible when a jet of hydrogen burns?

5   Why is the name *hydrogen* appropriate for this gas?

6   Write the word equation for the reduction of lead oxide with hydrogen. On this equation label the following: (*a*) the oxidizing agent (*b*) the reducing agent (*c*) the substance that is oxidized, (*d*) the substance that is reduced.

7   How are liquid oils changed to solid fats for cooking purposes?

8   What is water gas? How can it be obtained? What is meant by the 'water-gas shift' reaction?

9   Explain what is meant by each of the following, and give one example of each:
    a   oxidation
    b   reduction
    c   oxidizing agent
    d   reducing agent
    e   reversible reaction.

10  State three uses of hydrogen, apart from the one referred to in Question 7.

# 14
# Ammonia

## 1. Population and food shortage
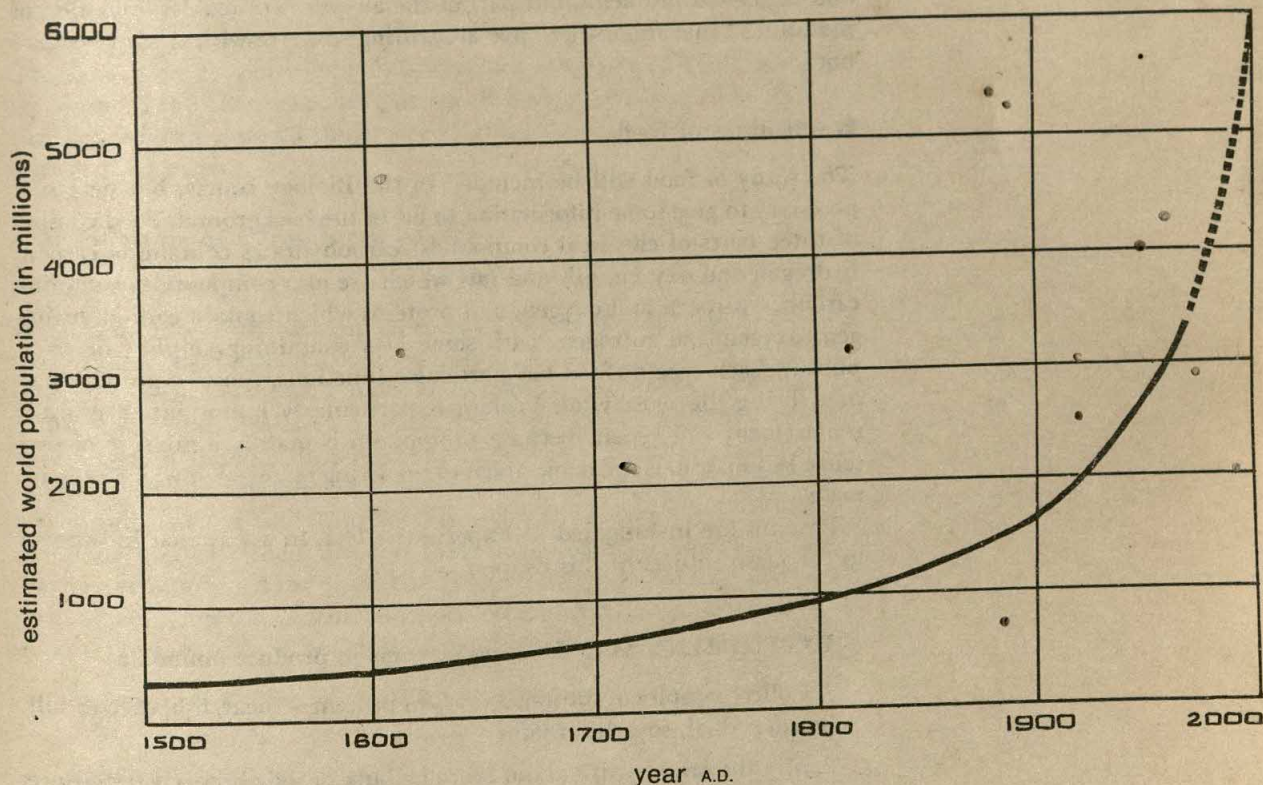
Fig. 14.1  **The Population Explosion**

'THERE is not enough food in the world for the people of the world — and there never has been. For hundreds of years there was a famine in some part of the world — on the average once every five years'. This statement appears in the Royal Society of Health Journal Volume 89/5, and it might seem a strange way in which to begin a chapter in a chemistry textbook. However, the theme of this particular chapter is the usefulness of chemistry and in particular the vital part which chemists are playing in solving the world food problem.

The magnitude of the problem can be highlighted by reference to Fig. 14.1, which shows the estimated world population from the year 1500 A.D. up to that predicted for 2000 A.D.

Clearly, since the beginning of the nineteenth century there has been a rapid increase in population. In this century the increase has been so rapid that much reference is made to the 'population explosion'. It is expected that the world's population will double in the next thirty years. It has been advances in medical science which have made a major contribution to population increase — fewer children die in infancy and adults live longer. At the same time, sciences associated with agriculture have made possible increased food production. Even so supply has not kept pace with demand and many countries suffer a chronic shortage. Scientists, including chemists, continue to apply their skills to food production and associated problems, but part of the answer is probably a question of morality so that those who have are willing to share with those who have not.

## 2. Chemistry of food

The study of food will be included in the Biology course, but here it is necessary to give some information to fill in the background. Food consists of three types of chemical compounds: carbohydrates containing carbon, hydrogen and oxygen, oils and fats which are also compounds containing carbon, hydrogen and oxygen, and proteins which contain carbon, hydrogen, oxygen and nitrogen, with some also containing sulphur or phosphorus. Each type of food has particular functions, those of proteins perhaps being the most vital. Protein is particularly important in growth, replacement and repair, because protoplasm is mainly a mixture of proteins. Protoplasm is the name given to the living material of which cells are made.

Proteins are investigated in Experiment 14.1, in a way that links them to the main subject of this chapter.

### EXPERIMENT 14.1   Heating proteins to produce ammonia

1. Collect samples of substances rich in protein — meat, fish, cheese, milk powder, dhal, soya bean flour.

2. Mix the sample with about twice its bulk of soda-lime. (Better results will be obtained if the sample is finely divided e.g. in powder form).

3. Place the mixture in a test tube and heat it.

4. Test the fumes given off with moist red litmus paper, and hold the stopper from a bottle of concentrated hydrochloric acid in the fumes. (WARNING: the fumes have an unpleasant smell, so the experiment should be carried out near an open window).

When the protein is heated with soda-lime it breaks down and gives off a mixture of substances in the fumes. Attention is focussed on just one of these substances which turns the moist red litmus paper blue, and gives dense white fumes when in contact with hydrochloric acid fumes. These

two reactions indicate the presence of *ammonia* gas, which was mentioned in the last chapter as a compound of nitrogen and hydrogen.
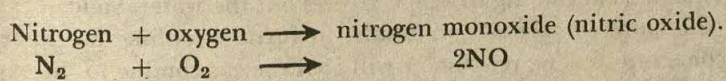
## 3. Importance of nitrogen compounds for food: fertilizers

Nowadays, ammonia is mainly converted into fertilizers which have to be added to the soil if it is going to give adequate crop yields. The use of ammonia in this way represents about a century of involvement by the chemist in the field of agriculture. During the nineteenth century the main elements necessary for normal plant growth became known, and it was shown that little growth occurred in the absence of nitrogen. Following up this work, it was demonstrated that certain compounds containing nitrogen could double the yield of cereal crops such as wheat. However, the chemical industry was also making demands on these same nitrogen compounds for making dyestuffs and explosives such as dynamite. The available nitrogen compounds were not abundant and by the end of the century, the then President of the British Association, Sir William Crookes, forecast a world shortage and pointed out the need to find new sources of nitrogen.

## 4. Manufacture of nitrogen compounds

### (i) *The Birkeland-Eyde process*

With four-fifths of the atmosphere known to be nitrogen, some method was required by which it could be fixed into compounds that could be used as fertilizers. As far back as the 1780's, Henry Cavendish (the discoverer of hydrogen) had suggested a direct combination between the nitrogen and oxygen of the air. In nature, this happens in association with lightning, so what was required was enough electrical energy to simulate a flash of lightning. At the beginning of this century Birkeland and Eyde, with cheap electricity at their disposal from hydro-electric power stations in Norway, accomplished the direct combination of nitrogen and oxygen. The process gave dilute nitric acid which was reacted with crushed limestone to produce *'nitrate of lime'* (calcium nitrate) containing 13% of nitrogen.

Nitrogen + oxygen $\longrightarrow$ nitrogen monoxide (nitric oxide).
$$N_2 + O_2 \longrightarrow 2NO$$

Nitrogen monoxide + oxygen $\longrightarrow$ nitrogen dioxide.
$$2NO + O_2 \longrightarrow 2NO_2$$

Nitrogen dioxide + warm water + oxygen $\longrightarrow$ nitric acid.
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Limestone + nitric acid $\longrightarrow$ nitrate of lime + carbon dioxide + water.
$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + CO_2 + H_2O$$
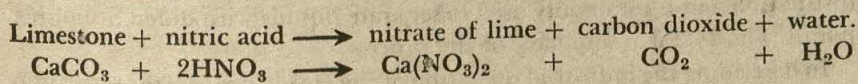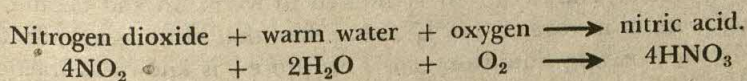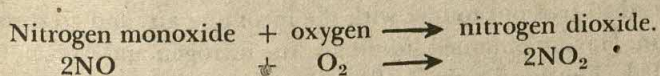
Limestone is cheap, and the air is free, but the electricity, even from a hydro-electric power station, is a very expensive item. This was also the drawback of the other process developed about the same time in France. Two of the raw materials, coal and limestone, were cheap but heavy demands were made on electricity and expensive pure nitrogen was

required. The product calcium cyanamide ($CaCN_2$) is a useful fertilizer containing about 20% nitrogen. Today it is still made for large scale agricultural use in Germany and Japan.

### (ii) *The Haber process*

The process which has largely superseded these earlier expensive methods went into commercial production in 1913. This was nine years after Fritz Haber had begun to study the problem and four years after Carl Bosch was given the job of turning a laboratory process into an industrial success. Haber was interested in combining nitrogen and hydrogen together to form ammonia.

$$\text{Nitrogen} + \text{hydrogen} \longrightarrow \text{ammonia.}$$
$$N_2 + 3H_2 \longrightarrow 2NH_3$$
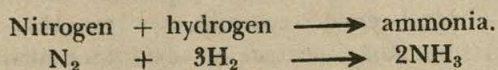
This reaction is, in fact, reversible so a balance is set up between the formation of ammonia and its breakdown into its elements. This balance is termed an *equilibrium*.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
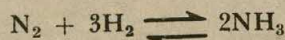
Haber demonstrated that the best yield of ammonia resulted from using a high pressure and low temperature. The difficulty with using a low temperature was that it took a long time to get any ammonia. Catalysts were developed by Bosch to speed up the process. Bosch also found out how to get hydrogen from water cheaply as described in the last chapter. A number of ways were used to get nitrogen from air, but now it is generally obtained from liquid air. Because of the very much increased demand for oxygen, one might almost consider nitrogen as a by-product from the liquefaction of air to get oxygen. Before outlining the manufacture of ammonia by the Haber Process, some consideration must be given to the liquefaction of air.

Air is filtered to remove the dirt and then compressed to 150 to 200 atmospheres (that is, a pressure 150 to 200 times greater than atmospheric pressure). Washing the air with sodium hydroxide solution then removes carbon dioxide and cooling to $-25°C$ freezes out the water. Sudden expansion of this pure compressed air results in further cooling and some air will become liquid. The remainder will cool the gas coming to the expansion chamber, then pass out to mix with the incoming air, and go through the cycle again. Having obtained liquid air, the nitrogen and oxygen have to be separated. The liquid air is allowed to warm up and because the boiling point of nitrogen ($-196°C$) is less than that of oxygen ($-183°C$) it boils off first leaving liquid oxygen. This process is known as fractional distillation and is commonly used to separate liquids with different boiling points. Fig. 14.2 is a summary of the process.

In describing the industrial operation of the Haber process, the operation of the Sindri plant provides the detail. Hydrogen from water gas and nitrogen from liquid air are mixed in the ratio 3:1 and compressed to 200 to 300 atmospheres. The compressed gases are then heated to about 550°C, passed over an iron catalyst containing traces of potassium and aluminium oxides which improve its activity. Some ammonia gas is formed and this

filtered air

compression

washing

cooling

expansion

liquid air    cold air

fractional
distillation

oxygen    nitrogen
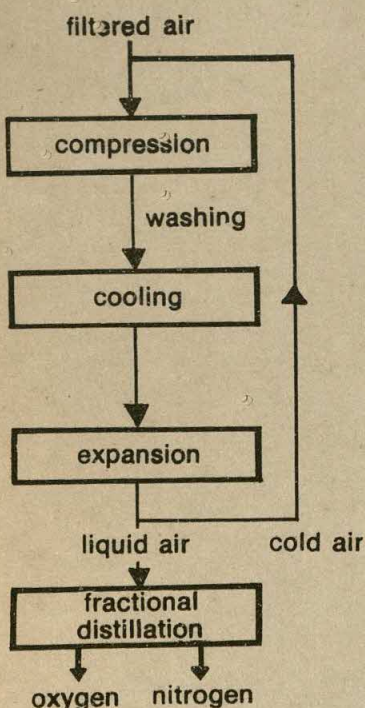
Fig. 14.2  **Liquefaction of Air**

is separated from unchanged nitrogen and hydrogen by liquefying it, and the nitrogen and hydrogen are recycled. Most of the ammonia produced in Sindri is converted to the fertilizer *sulphate of ammonia* (ammonium sulphate) which contains about 21% of nitrogen. Ammonia and carbon dioxide are passed through a suspension of calcium sulphate. Calcium carbonate is precipitated and then filtered off. The ammonium sulphate solution is carefully evaporated to dryness to give the solid.

Ammonia + carbon dioxide + calcium sulphate + water
$$2NH_3 \quad + \quad CO_2 \quad + \quad CaSO_4 \quad + H_2O$$
$$\longrightarrow \text{ammonium sulphate} + \text{calcium carbonate}$$
$$(NH_4)_2SO_4 + CaCO_3 \downarrow$$
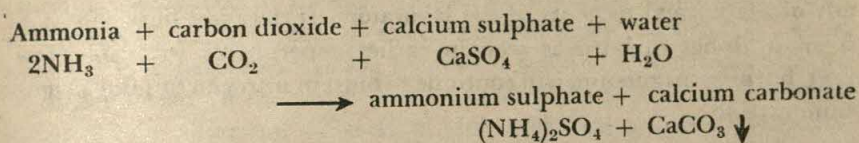
The more usual method of getting hydrogen is from hydrocarbons available from an oil refinery, as described in Chapter 14. This has resulted in the establishment of fertilizer plants alongside oil refineries and in some places a whole range of activities based on chemicals have arisen so that the term *petrochemical complex* is used. Chemicals from petroleum will be considered in detail later in the course, but some idea of the interplay of different factors involved in siting an industry is given in the following paragraphs.

## 5. Location of chemical industries

A plant for liquefying air could be put anywhere where there is electricity available to drive compression pumps. Since the oxygen in air is used for steel-making, a good place would be by a steelworks. But what about the nitrogen made available at the same time? This could be used up by building a fertilizer plant alongside the steel works, but then a source of hydrogen is required. If the hydrogen is produced by the Bosch Process, then the steel works and the Bosch Process are both making demands on the coke which might be available. Coke is obtained from coal and to avoid transport costs the steel works could be placed near a coal-field. In that case there would probably be a need to transport the iron ore to the steel works. This leads to a balancing of two cost items: will it be more expensive to take the coal to where the iron ore is mined or more expensive to take the iron ore to where the coal is mined?

Looked at in another way, suppose the starting point is the oil refinery. Where is it to be sited? Is it best located where most use can be made of the products? In such a case crude oil would have to be transported by pipeline or tanker. Or should the refinery be near the oil wells and the finished products transported to the users? With so much hydrogen available in the petroleum hydrocarbons, a fertilizer plant can be set up by the refinery. This uses nitrogen from liquid air, so this time there is the question of what to do with the oxygen. If transport facilities allow, then a steel plant could become part of the petrochemical complex. At the end of this chapter some questions are put, which when answered will give information about the siting of industries in this country, illustrating the points made here.

## 6. Properties and uses of nitrogen gas

So far, nitrogen has been considered in relation to ammonia, over 75% of the nitrogen made being converted into ammonia. It does have other properties and uses which are now described briefly before attention is again turned to ammonia. Nitrogen itself is rather dull with few reactions which can be seen in the school laboratory. It is a gaseous element with no colour or smell and it is only very slightly soluble in water. It does not react with any of the normal reagents in the laboratory. It does not burn, nor does it allow things to burn as seen in earlier experiments with air. However, burning magnesium will continue to burn in nitrogen forming magnesium nitride.

$$\text{Magnesium} + \text{nitrogen} \longrightarrow \text{magnesium nitride.}$$
$$3Mg + N_2 \longrightarrow Mg_3N_2$$
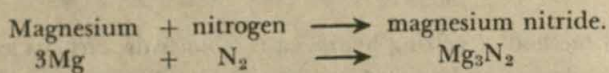
A number of industrial processes require the exclusion of oxygen, that is, an inert atmosphere. Nitrogen provides that inert atmosphere in the manufacture of semi-conductors (transistors), vitamin A and nylon. Liquid nitrogen is used as a refrigerating agent particularly for the storage of blood and corneas.
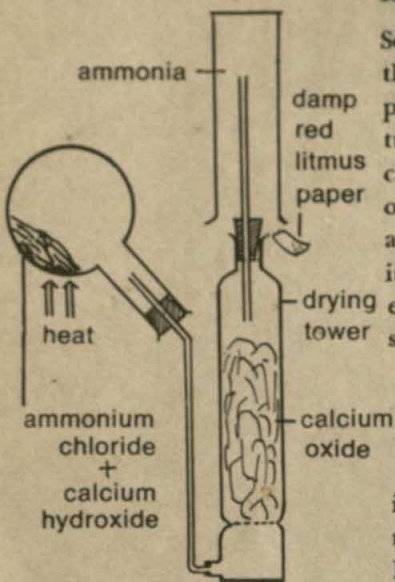


Fig. 14.3. Preparation of Ammonia

## 7. Laboratory preparation of ammonia

So that ammonia can be studied, it will be necessary to prepare some and this preparation is described in Experiment 14.2. The equation for this reaction is:

$$\text{Ammonium chloride} + \text{calcium hydroxide} \longrightarrow \text{calcium chloride} + \text{water} + \text{ammonia.}$$
$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3 \uparrow$$
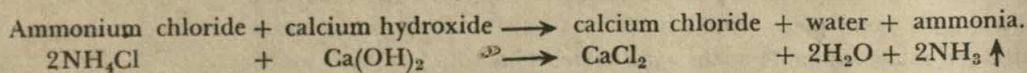
### EXPERIMENT 14.2  Preparation of ammonia

1. Mix together ammonium chloride and calcium hydroxide. Put the mixture in a flask, arranged as in Fig. 14.3.

2. Heat the flask gently and collect the gas by upward delivery. The gas jar is full when a piece of damp red litmus at its mouth turns blue.

## 8. Properties of ammonia

As with other gases, some of the properties of ammonia are also apparent as this method of preparation is studied. Ammonia is a colourless gas, lighter than air and with a smell which is characteristic (that is, it can be used to recognise ammonia because there is no other smell like it). Commonly, ammonia is said to have a *pungent* smell, which means the smell is biting. Experiment 14.3 gives a dramatic demonstration of another property of ammonia.
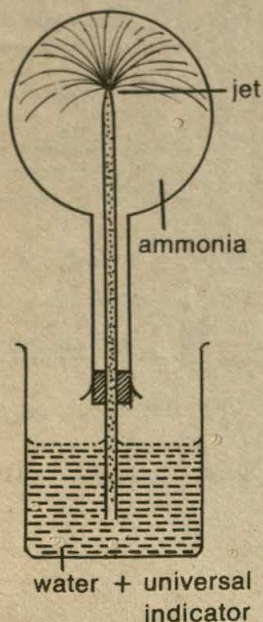


Fig. 14.4  The Fountain Experiment

### EXPERIMENT 14.3  The Fountain Experiment

1. Fill a large round-bottomed flask (500 cm$^3$ or larger) with dry ammonia.

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2. Put in a rubber bung with a glass jet which has just been dipped in water.

3. Quickly place the open end of the jet under the surface of some water in a beaker, to which has been added a few drops of Universal Indicator solution. (see Fig. 14.4).

Experiment 14.3 is known as the *Fountain Experiment* and the observations are explained by the ease with which ammonia dissolves in water. The drops of water originally at the end of the jet dissolve so much ammonia that the pressure inside the flask is reduced. The pressure of the air on the surface of the water forces liquid up the tube, so that it issues from the jet in a fountain. The use of Universal indicator in the fountain experiment shows that the solution of ammonia in water is weakly alkaline.
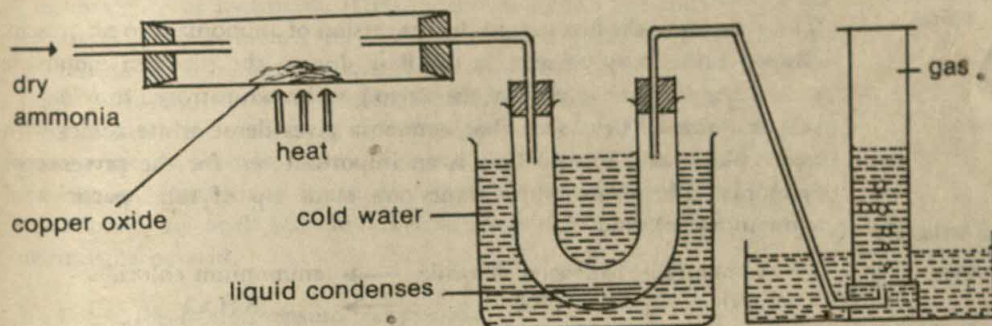


Fig. 14.5 **Reducing Action of Ammonia**

Three reactions of ammonia are of interest. Experiment 14.4 gives experimental evidence to support statements already made about the constitution of ammonia.

## EXPERIMENT 14.4

1. Using the apparatus shown in Fig. 14.5, pass dry ammonia over heated copper oxide.

2. Test the liquid which condenses in the U-tube with anhydrous copper sulphate.

3. Place a lighted splint in the gas.

In this experiment the anhydrous copper sulphate goes blue, showing that water is a product of the reaction. The oxygen comes from the copper oxide, but the hydrogen must have come from the ammonia. That the lighted splint goes out in the gas does not really prove anything but there is no simple test for nitrogen which the gas, in fact, is. This experiment shows by analysis that ammonia gas contains hydrogen and nitrogen. The equation for the reaction is:

Ammonia + copper oxide $\longrightarrow$ copper + water + nitrogen.

$2NH_3 + 3CuO \longrightarrow 3Cu + 3H_2O + N_2 \uparrow$
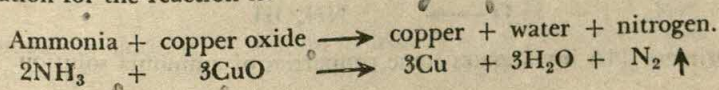
Experiment 14.5 shows on a small scale a reaction the full significance of which will be discussed in the next chapter.

### EXPERIMENT 14.5   The reaction of ammonia with oxygen

Put 25 cm³ of '880 ammonia' i.e. a solution of ammonia of density 0.880 g/cm³ into a wide-necked flask and warm it. Heat a platinum spiral until it is red hot and place it near to the surface of the ammonia (see Fig. 14.6). What evidence is there that a reaction is taking place?

In this experiment, platinum is acting as a catalyst for a reaction between ammonia and oxygen.

Ammonia + oxygen $\longrightarrow$ nitrogen monoxide + water.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
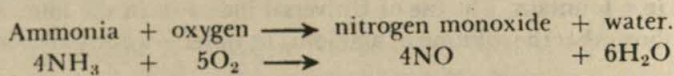
This reaction is the first step in the conversion of ammonia into nitric acid. (Brown fumes may be seen in the flask due to the nitrogen monoxide combining with the oxygen of the air to give brown nitrogen dioxide).

It has already been seen that ammonia gives dense white fumes with hydrochloric acid fumes. This is an important test for the presence of ammonia. The dense white fumes are made up of solid particles of ammonium chloride.

Ammonia + hydrogen chloride $\longrightarrow$ ammonium chloride.

$$NH_3 + HCl \longrightarrow NH_4Cl$$
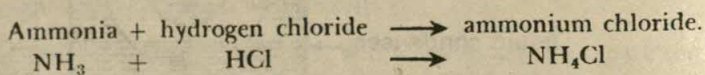
Hydrogen chloride is the gas in hydrochloric acid fumes.

### 9. Ammonium compounds

In writing the name of the product of the reaction between ammonia and hydrogen chloride the word *ammonium* has been used and the formula $NH_4$ given. Ammonia gas when bubbled into acids, neutralizes them (i.e. pH becomes 7) and compounds resembling sodium compounds are isolated. For example,

Ammonia + sulphuric acid $\longrightarrow$ ammonium sulphate.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
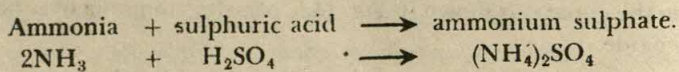
The resemblance of these compounds to sodium compounds leads to the use of the word 'ammonium'. A group of symbols of several elements appearing as one unit, common to a number of compounds, is known as a *radical*. $NH_4$ is the ammonium radical. Can you think of any other radicals which you have already come across?

Acids can also be neutralized by the solution of ammonia and attention is now turned to this solution which is known to be alkaline. Alkaline solutions encountered in Chapter 12 were solutions of hydroxides, so it is likely that ammonia reacts with water to form a hydroxide.

Ammonia + water $\longrightarrow$ ammonium hydroxide.

$$NH_3 + H_2O \longrightarrow NH_4OH$$

Experiment 14.6 investigates some properties of ammonia solution.



wooden rod

platinum spiral

880 ammonia solution
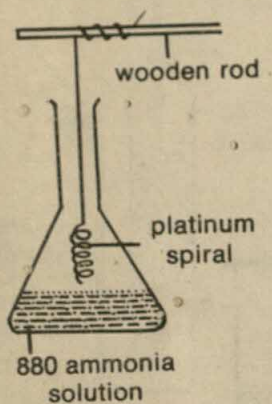
Fig. 14.6   **Catalytic Oxidation of Ammonia**

## EXPERIMENT 14.6   Properties of ammonia solution

(a) Heat a small quantity of ammonia solution in a test tube until no more liquid remains. Identify any gases evolved.

(b) Add ammonia solution drop by drop to small quantities of each of the following solutions contained in test tubes: iron sulphate, magnesium sulphate, copper sulphate and zinc sulphate.

In Experiment 14.6(a), nothing remains on heating which indicates that ammonium hydroxide does not exist as a solid. When the solution is heated, ammonia is given off, and the reaction given above can be considered to be reversible:

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$
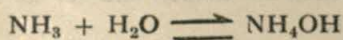
The existence of hydroxide (OH), is shown by the precipitation of the hydroxides of the metals used in Experiment 14.6(b). There are few ammonium hydroxide molecules in a solution of ammonia so the term ammonia solution is often preferred to ammonium hydroxide.

Ammonia solution is used as a household cleaner, being an effective grease remover. It is also a convenient source of ammonia in the laboratory. Ammonium compounds are usually formed by passing ammonia gas into the appropriate acid, but the alkaline ammonia solution could also be neutralized by acid.

## 10. Properties of ammonium compounds

Ammonium compounds are commonly white crystalline solids similar to common salt (sodium chloride). They are all soluble in water, and when heated they decompose easily.

## EXPERIMENT 14.7

1. Gently heat some ammonium chloride in the bottom of a beaker. (see Fig. 14.7). What do you see?

2. Allow the fumes given off to cool and notice the formation of a solid.



Fig. 14.7   Sublimation of Ammonium Chloride

Ammonium chloride is often considered as a substance which sublimes and certainly no liquid is observed in Experiment 14.7. However, the effect of heat is to decompose the solid, the products of decomposition being two gases, ammonia and hydrogen chloride. When the heat is removed re-combination takes place and the solid ammonium chloride results.

The other significant property of ammonium compounds has already been used in preparing ammonia. Universal indicator solution will show sodium hydroxide and calcium hydroxide solutions to be more alkaline than ammonia solution. These compounds which give very alkaline solutions are known as strong alkalis and when they react with ammonium compounds, ammonia gas is given off.

For example,

Ammonium chloride + sodium hydroxide ⟶ sodium chloride + water + ammonia

$$NH_4Cl \quad + \quad NaOH \quad \longrightarrow \quad NaCl \quad + H_2O + NH_3 \uparrow$$

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## 11. Uses of ammonium compounds

Ammonium compounds have some important uses. Ammonium sulphate is the most important fertilizer used in agriculture and ammonium nitrate is also used in this connection. Ammonium chloride is used in the manufacture of dry cells which are used for torches, transistor radios and other portable electrical equipment. Ammonium carbonate is the main constituent of smelling salts.

This chapter began with the world's food problem in mind and has been a study of the chemistry of ammonia. Without this knowledge a successful solution to the problem is not possible. The part played by the chemist in making a better world has been illustrated in this chapter and will continue to be highlighted throughout this book.

### Questions

1 What do you understand by the term 'population explosion'?

2 Find examples of the way in which medical science has decreased the death rate.

3 What is the importance of including protein in the diet?

4 At the end of the nineteenth century, a situation arose which could be referred to as the 'nitrogen problem'. What do you understand by the 'nitrogen problem'?

5 How did Fritz Haber solve the 'nitrogen problem'?

6 What were the contributions of Bosch to this solution?

7 Outline the process by which air can be liquefied and separated into nitrogen and oxygen.

8 Find out the sites of oil refineries in India. Why do you think these sites have been chosen?

9 It has been suggested that Haldia port, south of Calcutta, should be the site of a petrochemical complex. Suggest reasons why this would be a good idea.

10 'Nitrogen is inert'. Explain this statement.

11 What are the important uses of nitrogen?

12 Write an equation for a reaction by which ammonia can be prepared in the laboratory?

13 Describe and explain the Fountain Experiment in your own words.

14  How would you show that ammonia contains hydrogen?

15  You are given a mixture of ammonium chloride and sodium chloride (common salt) which are both soluble in water. How would you try to separate this mixture?

16  Describe two tests by which you could identify the gas ammonia.

# 15
# Nitric Acid
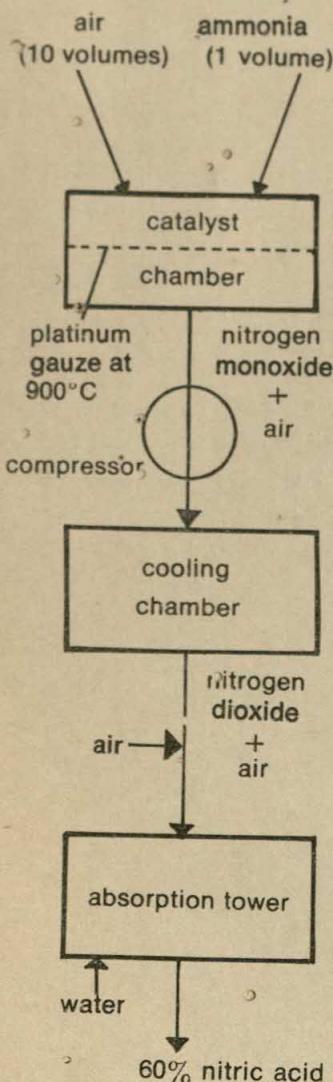
THIS chapter is linked with the previous one because much of the ammonia which is manufactured is converted into nitric acid. The reaction which is the starting point for this conversion has already been considered. Experiment 14.5 showed that in the presence of a heated platinum catalyst, ammonia is oxidized to nitrogen monoxide (nitric oxide). The industrial process which is based on this oxidation is known as the Ostwald Process.

## 1. Manufacture of nitric acid: The Ostwald Process

Ammonia is mixed with air in the ratio ten volumes of air to one volume of ammonia gas, and passed over platinum gauze, the temperature of which is maintained at around 900°C by the heat given out during the reaction.

Ammonia + oxygen ⟶ nitrogen monoxide + water.
$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$
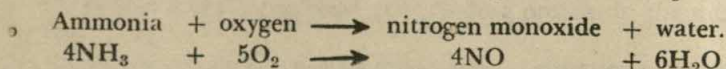
Compression of the gases, followed by rapid cooling, results in the combination of the nitrogen monoxide with further oxygen so that nitrogen dioxide is formed.

Nitrogen monoxide + oxygen ⟶ nitrogen dioxide.
$$2NO + O_2 \longrightarrow 2NO_2$$
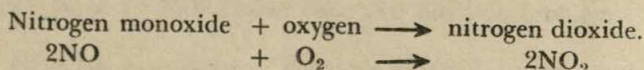
The nitrogen dioxide together with the remaining air (sometimes more air is added at this point) is passed up a tower, down which passes warm water. The product obtained at the bottom of the tower is about 60% nitric acid — this means 60 parts of anhydrous nitric acid ($HNO_3$) and 40 parts of water.

Nitrogen dioxide + oxygen + water ⟶ nitric acid.
$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$
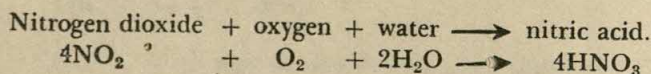
By ordinary distillation the acid concentration can be increased to about 70%, and this is the 'concentrated nitric acid' used in laboratories. Anhydrous nitric acid (pure nitric acid) can be obtained by distilling the 70% acid with concentrated sulphuric acid.

The Ostwald Process is the one adopted at the Sindri fertiliser plant. A simplified flow diagram of the process is given in Fig. 15.1.

## 2. Direct method of preparing nitric acid

There are occasions when anhydrous nitric acid is required, and although this can be obtained from the Ostwald Process as described above, there is



air
(10 volumes)

ammonia
(1 volume)

catalyst
chamber

platinum
gauze at
900°C

nitrogen
monoxide
+
air

compressor

cooling
chamber

nitrogen
dioxide
+
air

air ⟶

absorption tower

water

60% nitric acid

Fig. 15.1 **Flow diagram of the Ostwald Process**

also a direct method. The procedure goes back, at least, to the sixteenth
century and is there described as follows: 'Heat oil of vitriol (concentrated
sulphuric acid) with saltpetre (potassium nitrate) in a retort and distil into
a cooled vessel the vapours which arise.' Experiment 15.1 uses this method.

## EXPERIMENT 15.1  Laboratory preparation of nitric acid

1. Set up the apparatus as shown in Fig. 15.2.

2. Put 50 g of potassium nitrate into the retort, and cover it with con-
centrated sulphuric acid.

3. Heat the mixture so that it boils.

4. Pure nitric acid vaporizes from the mixture and is condensed in the
cooled flask.
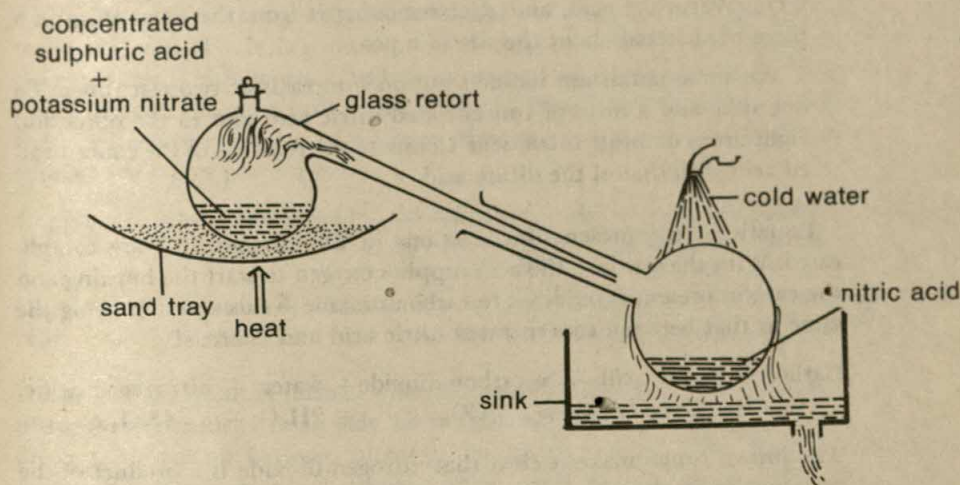


Fig. 15.2  **Preparation of Nitric Acid**

Potassium nitrate + sulphuric acid $\longrightarrow$ potassium hydrogensulphate + nitric acid.

$$KNO_3 \quad + \quad H_2SO_4 \quad \longrightarrow \quad KHSO_4 \quad + \quad HNO_3$$
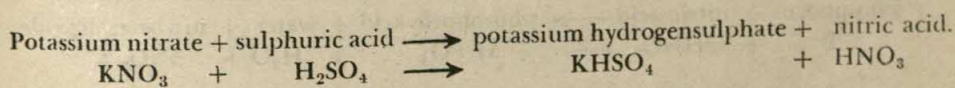
In the industrial preparation using this method, the apparatus may be of
stainless steel but, in this country, earthenware vessels are mostly used.
Potassium nitrate is available here in India, but elsewhere, the cheaper
sodium nitrate is used instead.

## 3. Properties of nitric acid

Pure nitric acid is a colourless, fuming liquid, but as prepared above it
may have a slight yellow colour. This is because even at room temperature
slight decomposition occurs in which nitrogen dioxide is formed. This
dissolves in nitric acid to give a yellow colour. The all-glass apparatus is
used because the pure acid attacks rubber and cork.

Besides nitrogen dioxide being formed when nitric acid decomposes,
oxygen is also liberated. Since nitric acid readily produces oxygen it behaves

as an oxidizing agent. This property is shown most vigorously by the pure acid, but the concentrated and dilute acids also act as oxidizing agents. Some of the reactions in which nitric acid acts as an oxidizing agent are investigated in Experiment 15.2.

### EXPERIMENT 15.2   Oxidizing action of nitric acid

1. Arrange some warm, dry sawdust in a pile. Pour 4-5 cm³ of pure nitric acid (from Experiment 15.1) onto the sawdust pile and stand well back from the apparatus since the reaction is very vigorous.

2. Take a piece of phosphorus about the size of a grain of rice and place it in a dry evaporating dish. Leave the phosphorus to dry for about a minute, then add 2-3 cm³ of pure nitric acid, and stand back.

3. Put concentrated nitric acid into a boiling tube to a depth of about 2 cm. Warm the acid, and after removing it from the flame drop in a piece of charcoal about the size of a pea.

4. Put some potassium iodide solution into each of two test tubes. To one tube add a drop of concentrated nitric acid and to the other add eight drops of dilute nitric acid. Compare the reaction of the concentrated acid with that of the dilute acid.

Equations to represent the reactions in Experiment 15.2 are complicated. With the sawdust, the acid supplies oxygen to start the burning and the carbon present is oxidized to carbon dioxide — this reaction being the same as that between concentrated nitric acid and charcoal.

Carbon + nitric acid $\longrightarrow$ carbon dioxide + water + nitrogen dioxide.
$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2 \uparrow$$
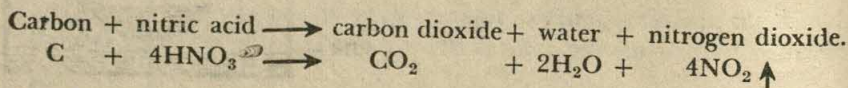
The brown fumes make it clear that nitrogen dioxide is a product of the reaction, as is also the case when phosphorus is oxidized. A simplified equation for this reaction is:

Phosphorus + nitric acid $\longrightarrow$ phosphoric acid + water + nitrogen dioxide.
$$P + 5HNO_3 \longrightarrow H_3PO_4 + H_2O + 5NO_2 \uparrow$$
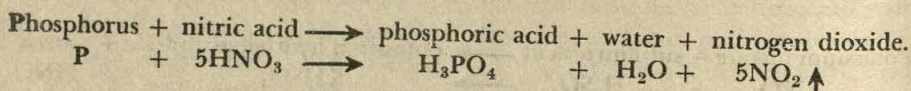
The dark coloration resulting from the reaction between nitric acid and potassium iodide solution is due to the formation of iodine. At this stage the equation is not given, but it should be noted that the liberation of iodine from potassium iodide solution is used as a test for oxidizing agents. The iodine liberated could be detected by its action on starch solution which it turns blue, but is easily recognised by its colour.

### 4. Reaction of nitric acid with metals

The reactions of nitric acid with metals are interesting because they do not fit into the pattern observed for other acids reacting with metals (see the next chapter). The reason for the exceptional behaviour of nitric acid is related to its oxidizing properties. In general, metals react with acids to produce hydrogen. Hydrogen is a reducing agent (see Chapter 13) which

will react with oxidizing agents such as nitric acid to form water. At the same time, the nitric acid is reduced, and a variety of products result — nitrogen dioxide, nitrogen monoxide, dinitrogen oxide ($N_2O$ — nitrous oxide) and even ammonia. The equations for the reactions chosen for investigation in Experiment 15.3 are relatively simple.

## EXPERIMENT 15.3   Reaction of nitric acid with copper

1. Place some copper turnings in a test tube and add about 2 $cm^3$ of dilute nitric acid.

2. Put a few copper turnings in a test tube and add several drops of concentrated nitric acid.

Is the reaction the same for both the dilute and the concentrated acids?

In both reactions copper nitrate is formed and this gives the blue colour to the solution. There is a gas evolved in each case. With the dilute acid the evolution is not vigorous, and the brown coloration of the vapour soon goes, although the gas is still being produced. With the concentrated acid, the familiar brown fumes of nitrogen dioxide are formed. The reactions which have taken place are:

Copper + (dilute) nitric acid $\longrightarrow$ copper nitrate + water + nitrogen monoxide.
$$3Cu \ + \ \ \ \ 8HNO_3 \ \ \ \ \longrightarrow 3Cu(NO_3)_2 \ \ \ + 4H_2O + 2NO \uparrow$$

Copper + (concentrated) nitric acid $\longrightarrow$ copper nitrate + water + nitrogen dioxide.
$$Cu \ \ + \ \ \ 4HNO_3 \ \ \ \ \ \longrightarrow \ Cu(NO_3)_2 \ \ \ \ \ + 2H_2O + 2NO_2 \uparrow$$
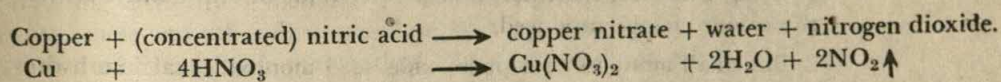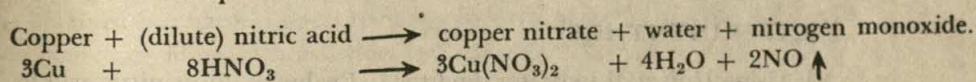
The gaseous product formed when dilute nitric acid reacts with copper, nitrogen monoxide, has already been encountered. It can be formed by direct combination between nitrogen and oxygen, and is also obtained when ammonia is oxidized catalytically in the Ostwald Process. It is a colourless gas, insoluble in water. On coming into contact with the oxygen of the air, it forms brown nitrogen dioxide.

Nitrogen monoxide + oxygen $\longrightarrow$ nitrogen dioxide.
$$2NO \ \ \ \ \ \ \ + \ O_2 \ \longrightarrow \ \ \ \ 2NO_2$$
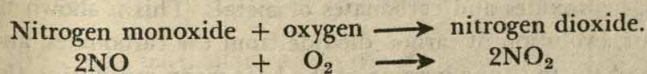
This accounts for the brown coloration seen originally when dilute nitric acid is added to copper turnings. As the nitrogen monoxide reaches the surface of the solution it combines with the oxygen in the air. As the air is swept from the test tube this reaction can no longer take place.

Nitrogen dioxide is already a very familiar gas having been encountered at the beginning of Chapter 3 when lead nitrate was heated, and in various other places since then. Its most obvious property is its brown colour. It is also very soluble in water giving an acidic solution. Care should be taken that it is not inhaled since it is liable to cause septic pneumonia.

The two gases, nitrogen monoxide and nitrogen dioxide, are significant only with regard to their intermediate part in the production of nitric acid, and of sulphuric acid by the lead-chamber process which will be considered in the next volume of this series.

Before passing to reactions in which nitric acid behaves like any other acid, an interesting effect of the acid is investigated in Experiment 15.4.

### EXPERIMENT 15.4  Action of nitric acid on protein

Take a slice of the white of a hard-boiled egg and add a drop of concentrated nitric acid to it. What do you see? Add some ammonia solution. What change now takes place?

The egg white is protein. The yellow stain, which is seen when the acid is brought into contact with the egg white, is typical of any protein and is used as a test for protein. Careless handling of nitric acid will result in similar yellow stains on the skin, which will in time be destroyed.

### 5. The 'acidic' reactions of nitric acid

Experiment 15.5 is carried out to show that there are some reactions in which dilute nitric acid, at least, behaves as a typical acid.

### EXPERIMENT 15.5

1. Using Universal indicator, find the pH value of dilute nitric acid by the colour change produced.

2. Put small amounts of copper oxide, lead monoxide, calcium hydroxide, copper carbonate, and sodium carbonate into separate test tubes. Add about 5 cm$^3$ of dilute nitric acid to each test tube. What happens? Test any gas evolved with limewater.

Feel the sides and bottom of the test tube.

From its pH value dilute nitric acid is clearly an acidic solution. It reacts with the oxides, hydroxides and carbonates of metals. This is shown by changes in colour, evolution of carbon dioxide from the carbonates, and the warming up of the test tube because of the heat given out during the chemical change. The equations for the changes taking place are:

Copper oxide + nitric acid $\longrightarrow$ copper nitrate + water.
$$CuO \quad + \quad 2HNO_3 \quad \longrightarrow \quad Cu(NO_3)_2 \quad + H_2O$$

Lead monoxide + nitric acid $\longrightarrow$ lead nitrate + water.
$$PbO \quad + \quad 2HNO_3 \quad \longrightarrow \quad Pb(NO_3)_2 \quad + H_2O$$
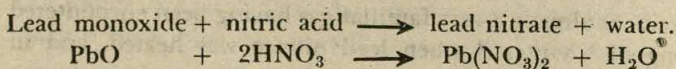
Calcium hydroxide + nitric acid $\longrightarrow$ calcium nitrate + water.
$$Ca(OH)_2 \quad + \quad 2HNO_3 \quad \longrightarrow \quad Ca(NO_3)_2 \quad + 2H_2O$$
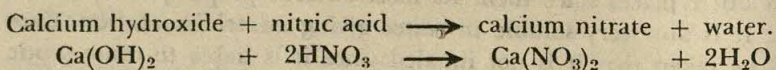
Copper carbonate + nitric acid $\longrightarrow$ copper nitrate + water + carbon dioxide.
$$CuCO_3 \quad + \quad 2HNO_3 \quad \longrightarrow \quad Cu(NO_3)_2 \quad + H_2O \quad + \quad CO_2 \uparrow$$
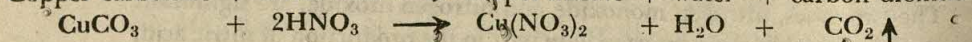
Sodium carbonate + nitric acid $\longrightarrow$ sodium nitrate + water + carbon dioxide.
$$Na_2CO_3 \quad + \quad 2HNO_3 \quad \longrightarrow \quad 2NaNO_3 \quad + H_2O \quad + \quad CO_2 \uparrow$$
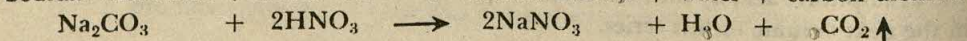
A careful look at these equations will reveal certain patterns, which will be investigated further in the next chapter since they are common to all substances called acids.

## 6. Uses of nitric acid

By reacting metals, metal oxides, hydroxides or carbonates, with nitric acid, a family of compounds known as 'nitrates' is obtained. The preparation of these nitrates is a major use for nitric acid. The nitrates of calcium, sodium, potassium and ammonium are all used as fertilizers. Ammonium nitrate is the most important of these since it contains about 35% of nitrogen. Used by itself it forms lumps and so powdered chalk is added to prevent this, the mixture being called *nitro-chalk*. Ammonium nitrate, potassium nitrate and glyceryl trinitrate are used in explosives which are considered below. Silver nitrate is used in photography.

The treatment of cellulose or cotton with nitric acid results in nitro-cellulose, and from this a number of useful products can be obtained. The lacquer on a car may be nitrocellulose lacquer. Artificial leather is made from cloth coated with nitrocellulose. Celluloid and photographic film are also obtained from nitrocellulose. The cotton from which nitrocellulose is obtained is a natural fibre. In many modern fabrics cotton is replaced by man-made fibres such as nylon and terylene. Nitric acid is used as an oxidizing agent in the manufacture of both these fibres. The colours with which these and other fibres are dyed may well have involved the use of nitric acid during their preparation. For example, starting with benzene from coal tar, nitrobenzene is formed by the action of pure nitric acid. This is then converted into aniline from which many important dyes, drugs and plastics are manufactured. The preparation of aniline dyes also involves the use of sodium nitrite ($NaNO_2$) which is obtained from sodium nitrate by the action of heat.

Sodium nitrate $\longrightarrow$ sodium nitrite + oxygen.

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$
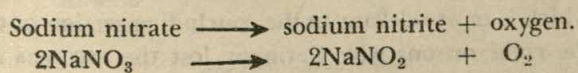
Nitric acid, particularly when concentrated, will attack most metals and so it is used to *etch* (eat into) them. For example, copper plates can be prepared from which pictures can be printed. The 'printed circuits' used in electronics can also be prepared by etching with nitric acid. The so-called noble metals gold, platinum and palladium are not ordinarily attacked by acids. A mixture of concentrated nitric acid and concentrated hydrochloric acid in the proportion 1 to 3 by volume dissolves these metals and because of this it is known as *aqua regia* — 'royal water'. Aqua regia plays an important part in the refining of these metals.

## 7. Use of nitric acid in explosives

One textbook of chemistry covering the uses of nitric acid gives almost exclusive consideration to explosives and dismisses fertilizers in one sentence. What are explosives? An explosive is a substance which undergoes rapid chemical change producing large volumes of gases when heated or

struck. The connection with nitric acid is that practically all modern explosives are made directly or indirectly from nitric acid.

Gunpowder which is a mixture of potassium nitrate, charcoal and sulphur is reputed to have been used by the Chinese from about 200 B.C. It still finds a use today for loosening coal in underground seams and for making fireworks. When ignited, the mixture burns rapidly releasing nitrogen and oxides of carbon and sulphur. The potassium nitrate is the source of oxygen, and gunpowder will burn in a vacuum.

Glyceryl trinitrate is better known as nitroglycerine. It is made by treating glycerol with a mixture of nitric and sulphuric acids. It is an oily liquid which is very sensitive to knocks so that it is very difficult to handle. It was Alfred Nobel who discovered how it could be handled more safely. His invention is known as *dynamite*, which is made by absorbing glyceryl trinitrate in sawdust mixed with sodium nitrate. Dynamite is especially useful for blasting rock. Nobel is remembered because the fortune he made from dynamite was used to found the Nobel Prizes in chemistry, physics, medicine, literature and peace.

To fill the shells used by the military, substances able to withstand the shock of propulsion must be used. The most commonly used substance of this type is trinitrotoluene, better known as TNT. Sometimes *Amatol* is used which is a mixture of ammonium nitrate with TNT.

Explosives are useful for blasting rock, digging ditches and tunnels and many other purposes involving the shifting of large quantities of rock and soil. Road-building projects or irrigation projects can be completed more rapidly if explosives are used to blast a way through. Unfortunately though, these peaceful uses of explosives are insignificant when compared to all that is required by Ordnance Factories throughout the world. For war, nitric acid is essential and it was the Haber Process linked with the Ostwald Process which enabled Germany to sustain World War I for so long even though previously vital supplies of sodium nitrate were cut off due to a blockade by the British Navy. L. F. Haber, the son of Fritz Haber, makes a comment which is most relevant to the concluding section of this chapter: 'One of the chief reasons why Germany lost the war was not through shortage of explosives but because the army took such a large share of the nitrogen compounds that there was not enough left for the farmers. In 1917 and 1918 the harvests were disastrously bad. Ironically, in the country where the solution to the nitrogen problem had been found, the wheat failed and people went hungry.'

Nitrogen compounds are essential to life and in order to increase food production they are used extensively as fertilizers. On the other hand nitrogen compounds destroy life and property when they are used in the weapons of war. In the case of potassium nitrate and ammonium nitrate, the same compound is used for both purposes. Glyceryl trinitrate is also interesting in this respect, since it is used as a medicine in heart trouble. The properties of these substances cannot be altered and it is right that they should be investigated. The fact that compounds of nitrogen have the potential to do good or to harm, illustrates the need for a scientist to consider his social responsibility. In the course of his investigations the scientist makes discoveries about the properties of substances. This know-

ledge is there for all to discover and nothing can stop man's quest to know more and more about his environment. It has been argued that once a scientist has announced his discovery to the world, his responsibility ceases. But the scientist is part of the world and as such he must retain an interest in the use to which his discovery is put. In this, of course, he is only one of many but this should not allow him to escape from his responsibility. Although science is an important aspect of modern life, it does not answer all questions. For example, if nitrogen compounds are considered, it might be asked, 'Is it right for nitrogen compounds to be turned into explosives when so many live at starvation level or below?' The answer to this question given by any individual would be far removed from science, although the individual might himself be a scientist. The question asked raises moral problems about right and wrong. Morality is not a matter of science, but an interplay of many and varied factors in society. The morality of one society may not be that of another and there is none who can say which society has the better morals. So, the choice between construction or destruction is made not on the basis of the accumulated scientific knowledge, but on what is believed to be right for a particular society at a particular time. The same choice has to be made with regard to the use of other products of nature or scientific invention — atomic energy, drugs and petroleum to quote but a few. The natural properties of these things cannot be altered, but the way in which they are used can be governed.

## 8. The nitrogen cycle
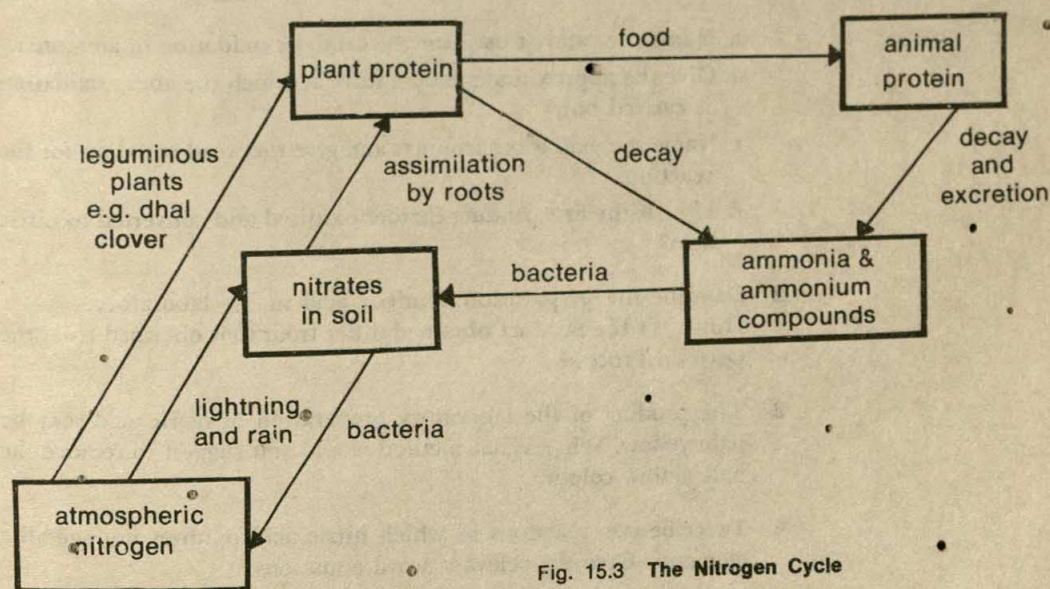


Fig. 15.3  **The Nitrogen Cycle**

In the natural course of events, nitrogen undergoes a series of changes into various compounds which, because they are continuously repeated, are called the nitrogen cycle. Fig. 15.3 gives a sample cycle for a system in which man is not involved, for example, in the middle of a jungle.

root crops ⎯⎯→ barley
e.g. potatoes      or oats

wheat ←⎯⎯⎯ clover,
                       dhal
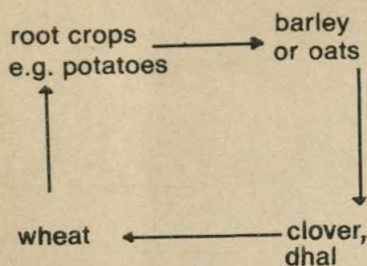
Fig. 15.4  **Rotation of Crops**

The nitrogen which the plant removes from the soil and builds into protein is returned to the soil directly when the plant dies and decays, or, indirectly, from the animal population dependent upon the plant. Atmospheric nitrogen is fixed by lightning as outlined in Chapter 14 but against this has to be balanced the effect of some bacteria which can release the nitrogen in nitrates back into the atmosphere. The presence of leguminous plants can be important since they are capable of making direct use of atmospheric nitrogen to build up proteins. When man comes on the scene, it is easy to see how the whole cycle can break down. When a crop is harvested, the plant is removed from the cycle and the nitrogen it has taken from the soil is not returned. The plant protein becomes human protein and this does not normally find its way back to the soil. One way of overcoming this difficulty is to grow a leguminous crop in the soil the next season to replenish the nitrogen. In fact, where crop rotation has been, or is, practised, it is four years before the same crop is again sown in a field (see Fig. 15.4).

With an increasing demand for cereal products such as wheat and rice, crop rotation does not seem to be the answer. The two previous chapters have shown that atmospheric nitrogen can be fixed by combination with hydrogen, and that from the ammonia so formed compounds can be obtained to replace the nitrates in the soil. So, with help from the chemist, the nitrogen cycle keeps turning.

**Questions**

1  a Name the catalyst used for the catalytic oxidation of ammonia.
   b Give the approximate temperature at which the above oxidation is carried out.
   c Name the oxidation products and give the word equation for the reaction.
   d How is the first product further oxidized and converted to nitric acid?

2  Describe the preparation of nitric acid in the laboratory.
   How does the product obtained differ from that obtained from the Ostwald Process?

3  The product of the laboratory preparation of nitric acid may be pale yellow. Why? What method would you suggest to remove the pale yellow colour?

4  Describe two reactions in which nitric acid oxidizes non-metallic elements. Give the relevant word equations.

5  Given copper turnings and nitric acid, describe briefly experiments by which you would show the formation of two different gases.

6  A careless laboratory worker has yellow stains on his fingers. What reason could you give for this and why?

7   Write out three equations for reactions in which copper nitrate is formed.

8   How is it possible for a thunderstorm to enrich the soil?

9   List the important uses of nitric acid.

10   A plant removes nitrogen from the soil. How is this replaced in uncultivated land? In cultivated land?

11   Show that nitric acid is necessary in peace and indispensable in war.

# 16
# Acids, Bases and Salts

## 1. The need for classifying compounds

WHEN the elements were introduced in Chapter 3 patterns were given in order to make it easier to appreciate the chemistry of some 105 different substances. The number of different inorganic compounds with which the chemist has to deal runs into many tens of thousands. Unless some classification system is introduced, not much can be learned about all these separate compounds.

Investigations of the solutions formed when oxides dissolved in water showed two different effects on substances known as indicators, e.g. litmus or Universal indicator. The soluble metal oxides gave alkaline solutions and the soluble non-metal oxides gave acidic solutions. Most metal oxides are insoluble, but otherwise they behave in the same way as the soluble ones. The general term used to include most metal oxides whether soluble or not is basic oxide. It is not only solutions of oxides which affect indicators. In Chapter 14 ammonia solution was seen to be alkaline, and in Chapter 15 the solution of anhydrous nitric acid (dilute nitric acid) was shown to be acidic.

The word 'salt' was used when the halogen family of elements was introduced. Halogen means 'salt-former' and comes originally from the name of the compound formed between sodium and chlorine — sodium chloride, known commonly as 'salt'. Sodium chloride is only one example of a wide variety of compounds having similar physical and chemical properties, all of which are grouped together as salts.

All this earlier work forms a foundation upon which can be built a classification system in which the important terms are *acids*, *bases* and *salts*. In this chapter, the meanings of these terms are investigated and compounds assigned to one or other of the classes.

## 2. Acids: Some general properties

*Acidus* is the Latin word for 'sour', and the term 'acid' was introduced into chemistry to name that group of compounds having a sour taste. Experiment 16.1 gives experience of this sourness. In this experiment and any others making use of acids, use a variety of the acids which are available to you. For example, dilute hydrochloric, dilute nitric, dilute sulphuric and dilute acetic acids together with tartaric and citric acids (solutions of these acids should both contain about 150 g of the solid per litre of water).

## EXPERIMENT 16.1   The taste of acids

1. Put one drop of acid (diluted as indicated above) into a test tube and add water to a depth of 1 cm.

2. Using a clean teat pipette, put a drop of the solution on the tongue at the edge towards the back.

3. When the taste has been noted, wash out the mouth and go on to the next acid.

*Note: This experiment should be carefully supervised.*

In this experiment, care has been taken to make the acid solutions dilute enough to prevent any harmful effects associated with other properties of the acids. The taste of citric acid may be familiar as the sour taste of limes, and it is also found in other citrus fruit. Acetic acid gives its taste to vinegar. In sour milk there is lactic acid and in rancid butter butyric acid. Many substances have this property of sourness and chemical analysis shows that they all contain acids. Using taste to identify substances can be dangerous, but fortunately acids have more in common than just their taste by which they can be identified, as is shown by the following experiments.
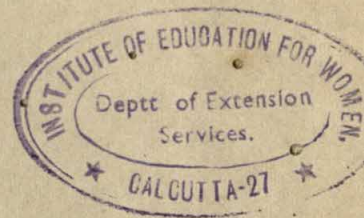
## EXPERIMENT 16.2   Action of acids on different indicators

1. Put a small quantity of acid into a test-tube. (Not more than 1 cm in depth).

2. Add two or three drops of litmus solution. Note the colour change, if any. Repeat with other acids.

3. Instead of litmus, use methyl orange and phenolphthalein and note the colour changes.

4. Test each acid with Universal indicator and take especial note of the pH in each case.

Draw up results in a table as shown.

| Indicator | Natural colour | Colour in acid |
|---|---|---|
| Litmus | | |
| Methyl orange | | |
| Phenolphthalein | | |

## 3. 'Strong' and 'Weak' Acids

All the acids affect these three indicators in the same way, although you may have noted that acetic, citric, and tartaric acids only just turn litmus red. The use of Universal indicator distinguishes more markedly between dilute nitric, hydrochloric and sulphuric acids on the one hand and acetic, citric and tartaric acids on the other. Dilute nitric acid, and the other two like it, is shown to be strongly acidic. The other three acids are only

weakly acidic. This observation leads to two sub-groups within the acid group — strong and weak acids. Besides this difference in their effect on Universal indicator, it will be seen that the reactions of the weak acids are slower than those of the strong acids. The terms 'strong' and 'weak' should not be confused with 'concentrated' and 'dilute'. Experiment 16.3 helps to make the differences clear.

## EXPERIMENT 16.3

1. Put a piece of zinc in a small quantity of concentrated sulphuric acid in a test tube. What happens?

2. Carefully pour the contents of the tube into about three times as much water. What happens now?

The concentrated sulphuric acid is a weak acid which is unable to react with the zinc very readily. Pouring the acid into water diluted it and increased its acid strength. Dilute sulphuric acid is a strong acid which reacts vigorously with zinc. This experiment is also an indication that water has a part to play in helping a substance to show its acid properties. In the case of citric and tartaric acids, this is even clearer because they are solids which have first to be dissolved in water before they show any acid properties. The anhydrous form of acetic acid is a liquid called 'glacial acetic acid' and if indicator paper is put into this, e.g. blue litmus paper, no change takes place. When the glacial acetic acid is put into water, it then turns blue litmus red in a typical acid reaction. We have found out now that acids are solutions of solids, liquids or gases in water, having certain properties such as sourness and a common effect on indicators.

## 4. Effect of acids on metals

The reaction of dilute sulphuric acid with zinc is another typical acid property and this is investigated in Experiment 16.4. In this experiment, dilute nitric acid is not used because its property of being an oxidizing agent, as seen in the last chapter, interferes with the normal acid reaction.

## EXPERIMENT 16.4

1. Put each of the acids into separate test tubes to a depth of about 2 cm.

2. Into each test tube of acid put 2 cm of magnesium ribbon. What happens?

3. Cover the top of the test tube with an empty test tube, *bottom down*, in order to trap any gas evolved. After about a minute, remove the covering test-tube and apply a lighted splint to the mouth of the other tube. What happens?

4. Repeat this experiment using different metals — a small piece of zinc, a short length of iron wire, a few copper turnings. If there is no reaction, or if the reaction is very slow, gently warm the test tube.

This experiment gives us two sets of information. The first set relates to acids and the second to differences between the activities of metals. Where the acids react with the metals, hydrogen is one of the products, so a general equation can be written:

$$\text{Metal} + \text{acid} \longrightarrow \text{hydrogen.}$$

This is true for all the acids investigated, but not for all the metals. Magnesium reacts quickly with all the acids, with zinc the reaction is slower, with iron heat is required to give a reasonable rate of reaction and in the case of copper no reaction takes place. This order of activity corresponds to that given in the Metal Activity Series introduced in Chapter 12, and is another example of the validity of that classification.

Although all the acids react with magnesium to give hydrogen, the reactions of the weak acids are slower than those of the strong acids. This supports the division of acids into these two groups — weak and strong.

Hydrogen has been identified as one of the products of the reaction between a metal and an acid, but what has happened to the metal involved in the reaction?

### EXPERIMENT 16.5

1. Put some dilute sulphuric acid into a small beaker and add zinc until no more will dissolve.

2. Filter the solution into an evaporating dish and evaporate to dryness, carrying out the last stages on a water bath.

In Experiment 16.5, the other product of the reaction between zinc and dilute sulphuric acid is isolated. It is a white crystalline solid which is known as zinc sulphate. Evaporating the solutions resulting from reactions between other metals and acids would also give solid products. These products contain the metal and a group of atoms from the acid. In fact, when the formula of the acid is compared with that of the solid product it is seen that the metal has taken the place of hydrogen. The compound formed when a metal replaces the hydrogen of an acid is a salt. The complete reaction between a metal and a dilute acid can now be represented by the following equation:

$$\text{Metal} + \text{dilute acid} \longrightarrow \text{salt} + \text{hydrogen.}$$
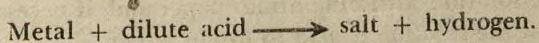
Some particular examples are:

$$\text{Iron} + \text{hydrochloric acid} \longrightarrow \text{iron chloride} + \text{hydrogen.}$$
$$\text{Fe} + 2\text{HCl} \longrightarrow \text{FeCl}_2 + \text{H}_2 \uparrow$$

$$\text{Zinc} + \text{sulphuric acid} \longrightarrow \text{zinc sulphate} + \text{hydrogen}$$
$$\text{Zn} + \text{H}_2\text{SO}_4 \longrightarrow \text{ZnSO}_4 + \text{H}_2 \uparrow$$

$$\text{Magnesium} + \text{acetic acid} \longrightarrow \text{magnesium acetate} + \text{hydrogen}$$
$$\text{Mg} + 2\text{CH}_3\text{COOH} \longrightarrow \text{Mg(CH}_3\text{COO)}_2 + \text{H}_2 \uparrow$$
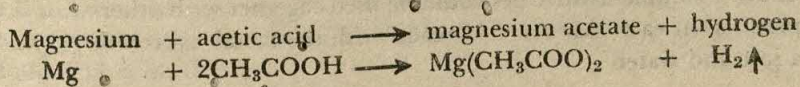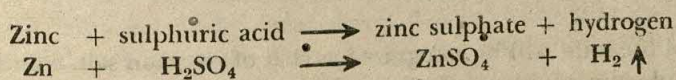
## 5. Reaction of acids with metal compounds

Acids not only react with metals, but also with certain metal compounds.

### EXPERIMENT 16.6   Reaction of dilute nitric acid with copper oxide

1. Put into a test tube enough copper oxide to fill the rounded bottom.

2. Add dilute nitric acid to a depth of about 2 cm. Warm gently to speed up the reaction. If all the copper oxide does not react, add a little more acid.

3. Repeat this experiment with other acids.

4. Other metallic oxides can be used as available.

As the copper oxide reacts with the acids, blue or blue-green solutions are formed. This colour of solution is typical of copper salts. The other product of this reaction is water, although it is difficult to demonstrate this because of the water already present. The general equation for Experiment 16.6 is:

$$\text{Metal oxide} + \text{acid} \longrightarrow \text{salt} + \text{water.}$$
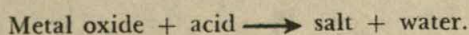
Equations for the reactions of nitric acid with copper oxide and lead monoxide are given in Chapter 15. Other examples are:

Copper oxide + sulphuric acid $\longrightarrow$ copper sulphate + water.
$\quad CuO \quad + \quad H_2SO_4 \quad \longrightarrow \quad CuSO_4 \quad + H_2O$

Copper oxide + hydrochloric acid $\longrightarrow$ copper chloride + water.
$\quad CuO \quad + \quad 2HCl \quad \longrightarrow \quad CuCl_2 \quad + H_2O$
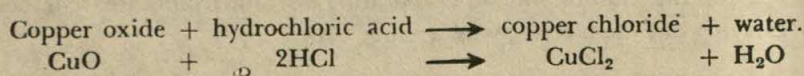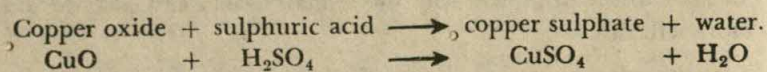
### EXPERIMENT 16.7   Reaction of dilute hydrochloric acid with sodium hydroxide

Use solutions of, as nearly as possible, equal strength.

1. Put 25 cm³ of dilute hydrochloric acid into a small beaker.

2. Add 25 cm³ of sodium hydroxide solution and mix the solutions by stirring.

3. Note the rise in temperature. What does this indicate?

4. Test the solution with blue litmus paper and, if necessary, add more acid so that the solution is acid to litmus paper.

5. Pour the solution into an evaporating dish and evaporate to dryness, heating gently, when nearly all the water has gone, to avoid spitting.

6. When the basin is cool, the white solid remaining can be tasted but only with your teacher's permission.

The taste of the solid will be recognized as that of common salt. Solutions of other soluble hydroxides could be used together with other acids if time permits. In each case the acid reacts with the metal hydroxide to produce a salt and water.

Metal hydroxide + acid $\longrightarrow$ salt + water.

For example:

Sodium hydroxide + hydrochloric acid $\longrightarrow$ sodium chloride + water.

NaOH + HCl $\longrightarrow$ NaCl + $H_2O$

Experiment 16.8 investigates the reactions of acids with the class of compounds known as carbonates.

### EXPERIMENT 16.8  Reactions of acids with carbonates

1. Put a small quantity of a carbonate (e.g. copper carbonate, sodium carbonate, calcium carbonate) into a test tube. Add a few drops of acid. What do you see?

2. Squeeze the bulb of a teat pipette and put it into the test tube. Release the bulb so that the gas evolved is sucked into the pipette. (Fig. 16.1)

3. Now squeeze out the gas through limewater. What do you see? What does this indicate?

4. This experiment can be repeated with any of the acids which have been under investigation.

Clearly the reaction which takes place between a carbonate and an acid releases carbon dioxide. Evaporating the solution to dryness would show that a salt had been formed, and water is also a product:

Carbonate + acid $\longrightarrow$ salt + water + carbon dioxide $\uparrow$.

As a result of Experiments 16.1 to 16.8, we know a lot more about what acids do. They taste sour, they affect indicators in a distinctive way, and, when dilute, they react with metals liberating hydrogen. They react with metal oxides and hydroxides forming salts and water only, and they react with carbonates to give salts, water and carbon dioxide. All this describes the way in which acids behave, but it does not say what acids are, nor does it explain why they show this common behaviour.



Fig. 16.1  Testing for Carbon Dioxide

### 6. Definition of an acid

Lavoisier noticed that when the oxides of non-metals dissolved in water they gave acidic solutions and assumed that all acids contained oxygen. In fact, it was on the basis of this assumption that he coined the name 'oxygen' which means 'acid-former'. The formula of hydrochloric acid has been given and the discovery of this acid and similar acids destroyed the 'oxygen-theory' of acids. The common feature of all the acids studied, is that they contain hydrogen. In their reactions with metals, metal oxides and hydroxides, and carbonates the hydrogen of the acid is replaced by a metal. Another feature of acids is that the properties are shown when there is water present but not otherwise. This information can be put together in the following definition:

123

*An acid is a compound which when dissolved in water has hydrogen available which can be replaced by a metal to form a salt.*

The form in which this hydrogen is available will be discussed at a later stage, when attention is given to the ways in which the atoms of elements combine together to form compounds. It is this 'available' hydrogen which accounts for the many common properties. In strong acids there is more 'available' hydrogen than in weak acids.

### 7. Bases: definition and properties

*A base is a compound which reacts with an acid to give a salt and water and no other product.*

Results of Experiments 16.6 and 16.7 show that metal oxides and hydroxides are bases: for example,

Copper oxide + sulphuric acid $\longrightarrow$ copper sulphate + water.
$$CuO \quad + \quad H_2SO_4 \quad \longrightarrow \quad CuSO_4 \quad + H_2O$$

Sodium hydroxide + hydrochloric acid $\longrightarrow$ sodium chloride + water.
$$NaOH \quad + \quad HCl \quad \longrightarrow \quad NaCl \quad + H_2O$$
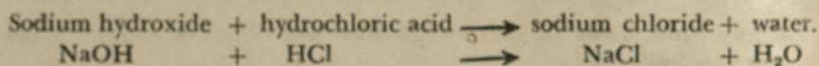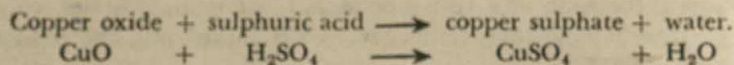
These equations indicate that bases are the oxides or hydroxides of metals. When a base reacts with an acid the reaction is called a *neutralization*.

$$Base + acid \longrightarrow salt + water$$
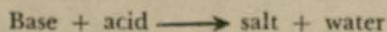
Potassium, sodium and calcium hydroxides are soluble and the solutions formed have a number of properties in common.

### EXPERIMENT 16.9 Action of metal hydroxide solutions on different indicators

1. Put a small quantity of sodium hydroxide solution into a test tube.
2. Add two or three drops of litmus solution. Note the colour change.
3. Repeat with other hydroxide solutions.
4. Instead of litmus, use methyl orange and phenolphthalein and note the colour changes.

Draw up the results in a table as shown.

| Indicator | Colour in metal hydroxide solution |
|---|---|
| Litmus | |
| Methyl orange | |
| Phenolphthalein | |

### 8. Alkalis

The blue colour seen when litmus solution is added to these metal hydroxide solutions, has already been encountered. A solution which turns litmus

blue is an *alkaline* solution. A substance, which when dissolved in water gives an alkaline solution, is called an *alkali*. Soluble bases such as sodium hydroxide are alkalis, and from Chapter 14 it is known that ammonia is also an alkali. The solution of ammonia in water turns litmus blue. If this solution is tested with Universal indicator, it is seen to be only weakly alkaline. Strong and weak alkalis exist, just the same as strong and weak acids.

Alkalis are neutralized by acids, the products being salt and water only. When finger tips are dipped into solutions of strong alkalis, and then rubbed together, a soapy, slippery feeling is experienced. The alkali attacks the skin — such an alkali is said to be *caustic*. The common names for sodium hydroxide and potassium hydroxide are *caustic soda* and *caustic potash* respectively.

Experiment 14.6(b) was used to show the presence of the hydroxide (OH) group in ammonia solution. If other metal hydroxide solutions are used, the same precipitates of insoluble hydroxides are formed. The hydroxide group is common to all alkalis, and the more of these hydroxide groups which are 'available' in an alkaline solution, the stronger the alkali.

The simplest definition of an alkali would seem to be that an alkali is a soluble base. It was suggested earlier that a base is a metal oxide or hydroxide but clearly this is not the case with ammonia. However, ammonia does react with acids to form salts. For example,

Ammonia + sulphuric acid $\longrightarrow$ ammonium sulphate.

$$2NH_3 \quad + \quad H_2SO_4 \quad \longrightarrow \quad (NH_4)_2SO_4$$
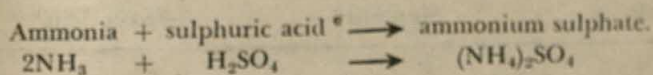
Water is not produced in this reaction, but the reaction is similar to that of other bases and ammonia solution does contain hydroxide groups like the soluble bases. So ammonia is also regarded as a base. This leads to the following definition of alkali:

*An alkali is a soluble base.*

## 9. Salts: definition and nomenclature

*A salt is a compound which can be formed by replacing the hydrogen of an acid with a metal.*

The name of a salt has two parts. The first part comes from the name of a metal or base:

$$\text{Magnesium} \longrightarrow \text{magnesium salts}$$

$$\text{Sodium hydroxide} \longrightarrow \text{sodium salts}$$

$$\text{Ammonium hydroxide} \longrightarrow \text{ammonium salts}$$

$$\text{Copper oxide} \longrightarrow \text{copper salts}$$

The second part usually ends in *-ate* and comes from the name of the acid, but salts formed from hydrochloric acid are called *chlorides*, and the ending *-ite* will sometimes be encountered. Common salt endings are listed below:

| | | | |
|---|---|---|---|
| hydrochloric acid | $\longrightarrow$ | chlorides | (Cl) |
| sulphuric acid | $\longrightarrow$ | sulphates | $(SO_4)$ |
| nitric acid | $\longrightarrow$ | nitrates | $(NO_3)$ |
| carbon dioxide solution | $\longrightarrow$ | carbonates | $(CO_3)$ |
| acetic acid | $\longrightarrow$ | acetates | $(CH_3COO)$ |
| sulphurous acid | $\longrightarrow$ | sulphites | $(SO_3)$ |

The available hydrogen in some acids, e.g. sulphuric acid, is not always completely replaced by metal so that the name of the salt includes hydrogen, and the salts are known as *acid salts*, e.g.

sodium hydrogensulphate $\quad NaHSO_4$ | also used are the names sodium bi-
sodium hydrogencarbonate $\quad NaHCO_3$ | sulphate and sodium bicarbonate

Experiments 16.4 to 16.8 all result in the formation of salts, and these provide the basis for standard methods of salt preparation. In considering the preparation of salts, it is useful to note that there are differences in their solubilities in water which influences the selection of the method used. This information is given in the following table (this relates to salts studied in this course):

| Salt | Solubility | Exceptions |
|---|---|---|
| Sodium, potassium and ammonium compounds | Soluble | |
| Nitrates | Soluble | |
| Hydrogencarbonates | Soluble | |
| Chlorides | Soluble | Silver, lead (soluble in hot water) |
| Sulphates | Soluble | Barium, lead, calcium (only slightly soluble) |
| Carbonates | Insoluble | Sodium, potassium, ammonium |

## 10. Preparation of soluble salts

### EXPERIMENT 16.10  Action of an acid on a metal

1. Half-fill a 100 cm³ beaker with dilute sulphuric acid and gently warm it.

2. Add small pieces of granulated zinc until no more will dissolve.

3. Filter the hot solution into an evaporating dish.

4. Carefully evaporate the solution to about half its bulk and then pour it into a crystallizing dish.

5. Cover the crystallizing dish and set it aside to allow time for the solution to cool and crystals to form.

6. When crystals have formed, decant the surplus liquid, wash the crystals and place them on a filter paper to dry.

The reaction, in this experiment, is represented by the equation

Zinc + sulphuric acid $\longrightarrow$ zinc sulphate + hydrogen.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$
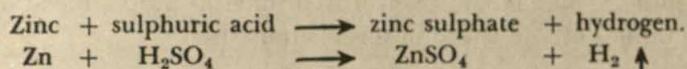
The crystals formed are hydrated zinc sulphate ($ZnSO_4.7H_2O$). The method can also be used to make crystals of iron sulphate ($FeSO_4.7H_2O$) and magnesium sulphate ($MgSO_4.7H_2O$).

### EXPERIMENT 16.11  Action of an acid on an insoluble metal oxide or hydroxide

1. Half-fill a 100 cm³ beaker with dilute nitric acid and gently warm it.

2. Add small quantities of lead oxide with constant stirring.

3. When no more oxide will react, filter the hot solution into an evaporating dish.

4. Proceed to obtain crystals as in Experiment 16.10.

Lead oxide + nitric acid $\longrightarrow$ lead nitrate + water.

$$PbO + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O$$
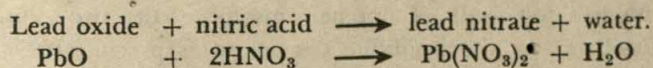
Copper sulphate could be prepared in this way from copper oxide and sulphuric acid. Zinc choride can be made from zinc oxide, magnesium sulphate from magnesium hydroxide and so on depending on availability of the bases.

### EXPERIMENT 16.12  Action of an acid on an insoluble carbonate

1. Put 100 cm³ of dilute sulphuric acid into a 250 cm³ beaker.

2. Add small quantities of copper carbonate until no more reacts.

3. Filter the solution into an evaporating dish.

4. Proceed to obtain crystals as in Experiment 16.10.

Copper carbonate + sulphuric acid $\longrightarrow$ copper sulphate + water + carbon dioxide.

$$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + H_2O + CO_2 \uparrow$$
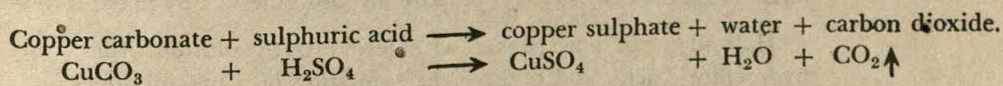
Blue hydrated copper sulphate crystals ($CuSO_4.5H_2O$) are obtained on crystallization. Calcium carbonate is a naturally occurring calcium salt which can be converted into the chloride or nitrate by this method. Magnesium, zinc and lead carbonates will also react with acids to give other

salts, although in the case of lead the method is only applicable to the preparation of lead nitrate.

## EXPERIMENT 16.13   The action of an acid on an alkali

The apparatus is set up as shown in Fig. 16.2.

(a) Place 25 cm³ of dilute sodium hydroxide solution in a conical flask and add a few drops of litmus. Run in dilute hydrochloric acid from a burette until the litmus just changes from blue to purple (neutral). Note the volume of acid added in this neutralization.

(b) Take another 25 cm³ of the same hydroxide solution, but this time without the litmus. Add the volume of acid required for neutralization. Transfer the neutral solution to an evaporating dish and proceed as in Experiment 16.10.

Sodium hydroxide + hydrochloric acid $\longrightarrow$ sodium chloride + water.

$$NaOH \quad + \quad HCl \quad \longrightarrow \quad NaCl \quad + H_2O$$
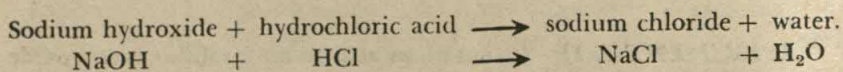
This method can be used for all sodium, potassium and ammonium salts. For ammonium salts, methyl orange should be used as an indicator instead of litmus.



burette

clamp

dilute hydrochloric acid

conical flask

Fig. 16.2   **Neutralizing a Soluble Base with Acid**

## 11. Preparation of insoluble salts

The methods of salt preparation given in Experiments 16.10 to 16.13 are only applicable to soluble salts. To prepare insoluble salts, two solutions are mixed together and the insoluble compound is precipitated. One solution contains the metal part of the salt and the other the acid part, e.g.,

Lead nitrate + sodium sulphate $\longrightarrow$ lead sulphate + sodium nitrate.

$$Pb(NO_3)_2 \quad + \quad Na_2SO_4 \quad \longrightarrow \quad PbSO_4 \downarrow \quad + \quad 2NaNO_3$$

Silver nitrate + hydrochloric acid $\longrightarrow$ silver chloride + nitric acid.

$$AgNO_3 \quad + \quad HCl \quad \longrightarrow \quad AgCl \downarrow \quad + \quad HNO_3$$

Barium chloride + potassium sulphate $\longrightarrow$ barium sulphate + potassium chloride.

$$BaCl_2 \quad + \quad K_2SO_4 \quad \longrightarrow \quad BaSO_4 \downarrow \quad + \quad 2KCl$$

Zinc sulphate + sodium carbonate $\longrightarrow$ zinc carbonate + sodium sulphate.

$$ZnSO_4 \quad + \quad Na_2CO_3 \quad \longrightarrow \quad ZnCO_3 \downarrow \quad + \quad Na_2SO_4$$
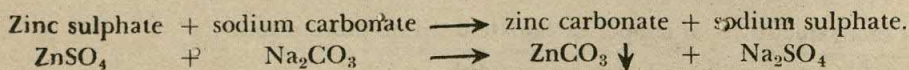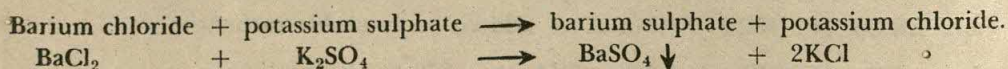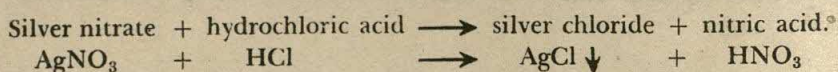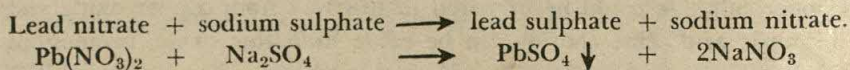
## EXPERIMENT 16.14   To prepare an insoluble salt by precipitation

1. Half-fill a 100 cm³ beaker with lead nitrate solution. Add dilute hydrochloric acid, and observe the formation of a precipitate.

2. Filter off the precipitate and to ensure the reaction is complete, add more acid to the filtrate. Filter this again if a precipitate occurs, and repeat the test until the filtrate no longer gives a precipitate when the acid is added to it.

3. Wash the residue with cold water and allow it to dry.

Lead nitrate + hydrochloric acid $\longrightarrow$ lead chloride + nitric acid.
$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$
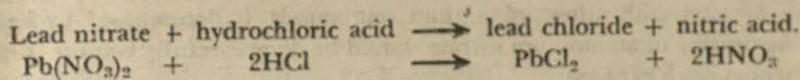
In the particular case of lead chloride, the precipitate can be put in a test tube with water and the mixture boiled. The hot solution can then be filtered and lead chloride crystals will form as the filtrate cools. The surplus liquid can be poured away and the needle-like crystals allowed to dry.

Sometimes salts which contain only two elements can be made directly from their elements. It has been mentioned earlier that sodium will burn in chlorine to form sodium chloride. Other metals will also form chlorides when heated in chlorine:

Sodium + chlorine $\longrightarrow$ sodium chloride.
$$2Na + Cl_2 \longrightarrow 2NaCl$$

Magnesium + chlorine $\longrightarrow$ magnesium chloride.
$$Mg + Cl_2 \longrightarrow MgCl_2$$

Aluminium + chlorine $\longrightarrow$ aluminium chloride.
$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$
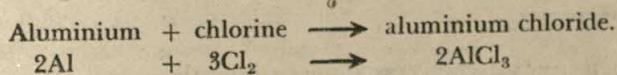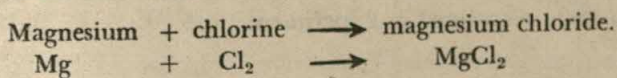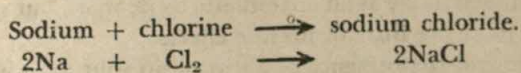
Iron sulphide is the iron salt of hydrosulphuric acid ($H_2S$) and it is formed when iron and sulphur are heated together.

Iron + Sulphur $\longrightarrow$ Iron sulphide.
$$Fe + S \longrightarrow FeS$$
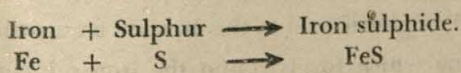
## 12. Properties of salts

The properties of the many thousands of salts which are known differ widely, so that for the class as a whole, no general properties can be listed. Attention is given instead to the groups such as carbonates, sulphates, nitrates and so on. The solubility table already given is an example of this approach. The properties of a group of salts are used in order to identify that group and this chapter concludes with a consideration of the ways in which the presence of various salts can be indicated.

The changes brought about by heat have already been introduced and their usefulness in analysis was mentioned (see Chapter 9).

### (i) Nitrates

Think of what happens when nitrates are heated — all produce oxygen which will relight a glowing splint; most also produce the brown gas nitrogen dioxide which is instantly recognisable. So, if a salt is heated and these observations are made, it can be said that the salt is a nitrate:

Metal nitrate $\longrightarrow$ metal oxide + oxygen + nitrogen dioxide.
$$2M(NO_3)_2 \longrightarrow 2MO + O_2 + 4NO_2 \uparrow$$
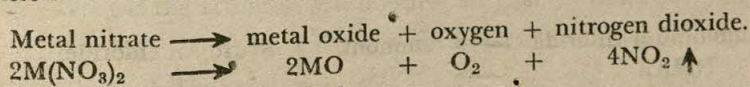
The nitrates of sodium and potassium give only oxygen on heating.

Sodium nitrate $\longrightarrow$ sodium nitrite + oxygen.
$$2NaNO_3 \longrightarrow 2NaNO_2 + O_2 \uparrow$$
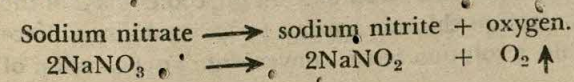
The only nitrate not included in this scheme is ammonium nitrate, which, in common with other ammonium compounds, is decomposed by heat. The heating of ammonium nitrate should be done carefully because it has a tendency to explode.

$$\text{Ammonium nitrate} \longrightarrow \text{water} + \text{dinitrogen oxide}$$
$$NH_4NO_3 \longrightarrow 2H_2O + N_2O$$
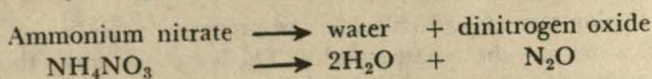
The dinitrogen oxide (nitrous oxide) is an interesting compound. It relights a glowing splint like oxygen, but can be distinguished from oxygen because oxygen gives brown fumes with nitrogen monoxide which dinitrogen oxide does not. Dinitrogen oxide is probably better known as 'laughing gas'. When inhaled, it causes unconsciousness and people have acted strangely when recovering from its effect, including laughing hysterically — hence the name. It is still used today as an anaesthetic by dentists, but since it is mixed with oxygen there are little or no side effects.

All nitrates are soluble and the presence of a nitrate in solution can be shown by the procedure outlined in Experiment 16.15.

### EXPERIMENT 16.15

1. Place a small iron sulphate crystal on a white tile. .

2. Cover the crystal with a drop of test solution (any nitrate could be used, but sodium nitrate solution is convenient).

3. Add a drop of concentrated sulphuric acid to the mixture on the tile.

4. Note the colour of the ring which forms round the iron sulphate crystal.

### (ii) Carbonates

All carbonates give off carbon dioxide when dilute nitric acid is added to them and most give off the same gas when heated.

$$\text{Carbonate} + \text{nitric acid} \longrightarrow \text{nitrate} + \text{water} + \text{carbon dioxide.}$$
$$MCO_3 + 2HNO_3 \longrightarrow M(NO_3)_2 + H_2O + CO_2\uparrow$$

$$\text{Carbonate} \longrightarrow \text{oxide} + \text{carbon dioxide.}$$
$$MCO_3 \longrightarrow MO + CO_2\uparrow$$
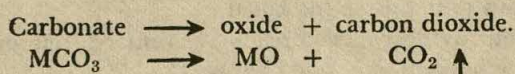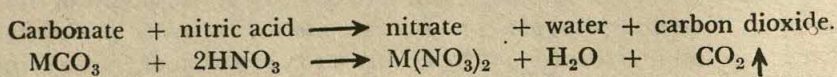
The exceptions to the action of heat are sodium and potassium carbonates which are not decomposed by heat.

### (iii) Chlorides

Chlorides are not effected by heat except for ammonium chloride which decomposes:

$$\text{Ammonium chloride} \longrightarrow \text{ammonia} + \text{hydrogen chloride.}$$
$$NH_4Cl \longrightarrow NH_3 + HCl$$
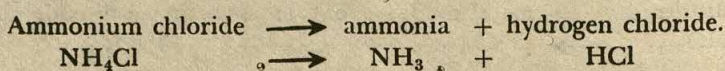
The ammonia and hydrogen chloride recombine on the cooler parts of the test tube, so that the ammonium chloride appears to have sublimed. Since most chlorides are soluble, a solution test is convenient. To a solution of

the known salt, dilute nitric acid is added, followed by silver nitrate solution. A white precipitate indicates the presence of a chloride.

Chloride + silver nitrate $\longrightarrow$ nitrate + silver chloride.

$MCl$ + $AgNO_3$ $\longrightarrow$ $MNO_3$ + $AgCl \downarrow$
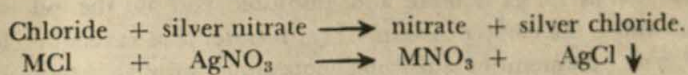
The nitric acid stops other insoluble silver compounds being precipitated, thus making the test one which only works for chlorides.

### (iv) *Sulphates*

Sulphates are not normally affected by heat, although iron sulphate is decomposed when heated strongly. The simple test for sulphates is to make a solution of the solid and then to add dilute hydrochloric acid followed by barium chloride solution. A white precipitate indicates the presence of a sulphate.

Sulphate + barium chloride $\longrightarrow$ chloride + barium sulphate.

$MSO_4$ + $BaCl_2$ $\longrightarrow$ $MCl_2$ + $BaSO_4 \downarrow$
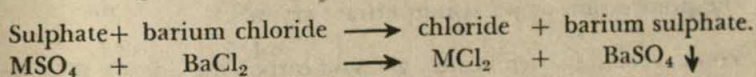
In this test, the hydrochloric acid prevents other barium compounds being precipitated, so it is distinctive for sulphates.

With the information that has now been given, it should be possible for you to take unknown salts and to find out whether they are nitrates, carbonates, chlorides or sulphates. This is an example of qualitative analysis — finding out what a substance contains.

## Questions

1  When solid A burned in oxygen a gas B was formed. This gas dissolved in water producing a solution which turned litmus red. What can be said about the nature of A and B?

2  When Universal indicator is added to dilute sulphuric acid and to citric acid, the colours obtained are not the same. Explain why this is so.

3  Write word equations for the action of each of the following substances on hydrochloric acid: magnesium, sodium hydroxide, copper oxide.

4  Describe how the reactions of the metals magnesium, zinc, iron, and copper with dilute hydrochloric acid can be used to put them in order of activity.

5  What is the action of dilute nitric acid on (*a*) zinc oxide, (*b*) zinc carbonate? Give the relevant word equations.

6  Give a definition of an acid.

7  What is an alkali? How does an alkaline solution affect (*a*) methyl orange, (*b*) phenolphthalein? What group of atoms is common to all alkaline solutions?

**8**  Frame a definition of an *acid salt*.

**9**  Make the headings 'Soluble' and 'Insoluble' and put the following salts under the correct heading: lead nitrate, lead carbonate, lead sulphate, ammonium sulphate, potassium sulphate, potassium chloride, silver chloride, silver nitrate, copper carbonate, calcium hydrogencarbonate.

**10**  Outline the preparation of crystalline iron sulphate ($FeSO_4 . 7H_2O$) from iron. Give the word equation for the reaction.

**11**  Outline, giving essential practical details and the word equation, the preparation of hydrated copper chloride from copper oxide.

**12**  Describe, giving the word equation and essential practical details, the preparation of potassium nitrate crystals.

**13**  Zinc carbonate, when heated, gives off carbon dioxide. Outline two methods, giving the word equations, by which crystals of zinc sulphate could be obtained from zinc carbonate.

**14**  How would you prepare:

**a**  barium sulphate from barium chloride,

**b**  magnesium carbonate from magnesium sulphate?

Give the relevant word equations.

**15**  Describe how lead chloride could be prepared from lead monoxide, dilute nitric acid, and sodium chloride. Give word equations.

**16**  If you knew that four unlabelled bottles contained distilled water, dilute nitric acid, dilute sulphuric acid and limewater (calcium hydroxide solution), describe how you would do a series of tests to find out which was which.

**17**  You are given three white crystalline solids — sodium nitrate, zinc nitrate, and zinc sulphate. How would you distinguish between them?

**18**  A, B, C, D and E are substances treated as shown below. Study the sequences of word equations and name one substance to which the equations could apply.

**a**  A is an element:

$$A + oxygen \longrightarrow oxide$$
$$oxide + water \longrightarrow solution$$
$$solution + litmus \longrightarrow blue\ colour.$$

**b**  B is an element:

$$B + oxygen \longrightarrow oxide$$
$$oxide + water \longrightarrow solution$$
$$solution + litmus \longrightarrow red\ colour.$$

**c  C is an element:**

$$C + \text{oxygen} \longrightarrow \text{oxide}$$
$$\text{oxide} + \text{water} \longrightarrow \text{no change}$$
$$\text{oxide} + \text{nitric acid} \longrightarrow \text{nitrate.}$$

**d  D is a compound:**

$$D + \text{water} \longrightarrow \text{solution}$$
$$\text{solution} + \text{sulphuric acid} \longrightarrow \text{sulphate.}$$

**e  E is a compound:**

$$E + \text{water} \longrightarrow \text{solution}$$
$$\text{solution} + \text{sodium hydroxide} \longrightarrow \text{sodium salt.}$$
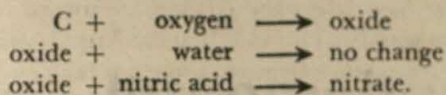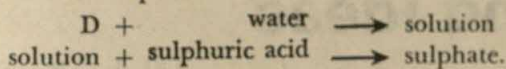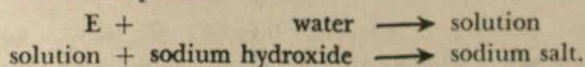
**19**  Study the following list of substances:

| | | |
|---|---|---|
| air | copper | sodium hydroxide |
| chlorine | sulphur | sea water |
| zinc | soil | copper oxide |
| oxygen | iron | hydrochloric acid |
| gold | copper sulphate-5-water | nitrogen |
| carbon | nitric acid | sulphuric acid |
| lead | anhydrous calcium chloride | mercury |

These substances are either:

**a** acids

**b** bases

**c** salts

**d** metallic elements

**e** non-metallic elements

**f** mixtures.

(i) Write down these six headings and place each substance in its correct list.

(ii) Which list contains a deliquescent substance?

(iii) Which list contains malleable substances?

(iv) Why is mercury the odd one out in its list?

(v) In which list does each substance contain hydrogen atoms in its molecules?
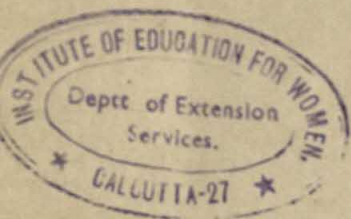
# 17
# Some Fundamental Laws and Ideas

In Chapter 8 of this book, the smallest particle of an element was called an 'atom'. The use of this word in that context was attributed to John Dalton. It is one aim of this chapter to consider the contribution of Dalton to the advance of Chemistry. However, Dalton's work cannot be considered in isolation. He constructed his Atomic Theory not only from the results of his own investigations, but also to explain the observations of others made over a period of about two centuries. By the time of Dalton these observations had been put together and briefly stated as laws. In Science, this is simply what a law is — a brief statement of the way in which matter behaves. Such a law is based on experiments carried out at different times and in different places all giving the same results. Once a law is established, it becomes useful in predicting results of similar experiments. If such predictions are not fulfilled, it does not necessarily mean that the law must be wrong. Instead, an investigation is set in motion to find the reasons why there has been an apparent violation of the law. Searches of this kind have in themselves resulted in important discoveries, but that is another story.

In this chapter, we are going to investigate two fundamental laws of chemistry. It is possible that our results may not agree exactly with the statement of these laws. Will this mean that we have disproved the laws? The answer is a firm 'No!' What then could be the reason for our results not agreeing with the laws? The most probable answer is that the balance which is used is not sufficiently accurate. Another reason could be lack of skill in the experimenter. Also, the time available to us is limited. One German professor, H. Landolt, worked for fifteen years to show the precise nature of the first law we are going to look at. "

### 1. Law of Conservation of Mass

The law to which Landolt devoted so much time is known as *The Law of Conservation of Mass*. In its simplest form this law can be stated as: *matter can neither be created nor destroyed*. This idea of the indestructibility of matter was held as far back as the time of Van Helmont, but it was Lavoisier, about two hundred years later, who put the idea into words: '..... nothing is created in the working of nature, and it can be taken as a law that in every operation an equal quantity of matter exists both before and after the operation. The whole art of making experiments in chemistry

is founded on this principle: we must always suppose an exact equation between the constituents of the body examined and those of the products of its analysis.' Experiments 17.1 and 17.2 can be carried out as demonstrations of the general truth of Lavoisier's statement. Experiment 17.1 is similar to one carried out by Lavoisier, and Experiment 17.2 is modelled on those of Landolt.

## EXPERIMENT 17.1

1. Put some sand in the bottom of a 250 ml round-bottomed flask.

2. Drop a small piece of white phosphorus onto the sand and tightly stopper the flask with a rubber bung, as shown in Fig. 17.1.

3. Weigh the flask and then warm it gently until the phosphorus catches fire.

4. When the reaction has ceased, allow the flask to cool and weigh it again.

*Note:* This experiment should be carried out by the teacher.



Fig. 17.1   Heating phosphorus in a closed flask

## EXPERIMENT 17.2

1. Have available solutions of: magnesium sulphate and barium chloride, lead nitrate and potassium iodide, silver nitrate and potassium chromate.

The solutions above are grouped in pairs.

2. Take a conical flask (preferably 100 cm³ size) and pour in enough of one of the solutions to just cover the bottom.

3. Tie a piece of cotton round the open end of a small test-tube (ignition tube) and half-fill it with the other solution of the pair.

4. Support the small test tube inside the conical flask as shown in Fig. 17.2. Weigh the whole apparatus.

5. Tip the flask so that the reagents mix.

6. Allow the flask to cool back to room temperature, and then weigh it again.



Fig. 17.2   Precipitation Reactions

It hardly needs to be said that the changes taking place in these experiments are chemical changes. Because of this, and also because of the discoveries in this century that matter can be converted to energy in nuclear reactions, the law of conservation of mass is now restated as follows:

*In a chemical reaction the total mass of the reacting substances is equal to the total mass of the products.*

## 2. Law of Constant Composition

In Chapter 8, the first characteristic of a compound was given as 'the composition of a compound is fixed'. From the eighteenth century onwards chemists concerned with making quantitative investigations (investi-

gations involving amounts of substances) appear to have assumed that compounds were of definite composition. The name associated with the systematic investigation of the composition of compounds is the French chemist Proust. He recognized the *Law of Constant Composition* in 1797, and stated it as follows: '*a compound is a substance to which Nature assigns fixed ratios.*' The way in which the truth of this law can be demonstrated is to prepare a compound in as many different ways as possible, and then to analyse each sample of the compound. Experiment 17.3 describes methods of preparing copper oxide from copper, and Experiment 17.4 shows how the copper oxide can be analysed.

## EXPERIMENT 17.3  Different methods of preparing copper oxide

Dissolve about 5 g of copper turnings in concentrated nitric acid. Divide the resulting solution of copper nitrate into three portions.

(a) Boil the solution to drive off water and then heat strongly to decompose the crystals. When there is no further loss of weight on heating, put the copper oxide sample in a dessicator (Fig. 17.3). Call it sample A.

(b) Add sodium carbonate solution. Filter off the copper carbonate which is precipitated. Heat the copper carbonate until there is no further loss in weight. Put the resulting copper oxide in a dessicator. Call it sample B.

(c) Add sodium hydroxide solution to precipitate copper hydroxide. Filter off the precipitate and heat it until there is no further loss in weight. Put the sample of copper oxide in a dessicator. Call it sample C.
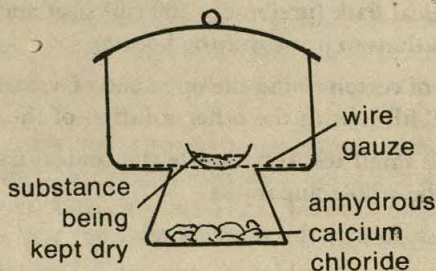


Fig. 17.3  **A Dessicator**

## EXPERIMENT 17.4  Analysing copper oxide

1. Weigh a porcelain boat. Into it put sample A and re-weigh.

2. Put the porcelain boat into a hard glass tube as shown in Fig. 13.3.

3. Heat the oxide and pass hydrogen over the heated oxide to reduce it.

4. When the reaction is complete, allow the metal to cool in the stream of hydrogen. When cool, weigh the boat and contents again.

5. As a check that the reaction is complete, put the boat back into the hard glass tube and heat it again for a short period in the stream of hydrogen. When cool, re-weigh the boat. If the reaction is complete, this weight will be the same as before.

6. The same procedure should be adopted with the other two copper oxide samples.

An example of the sort of results which might be obtained is given below:

| Sample | Weight of sample | Weight of copper |
|---|---|---|
| A | 1.39 g | 1.11 g |
| B | 1.43 g | 1.15 g |
| C | 1.51 g | 1.20 g |

Sample A:  $\% \text{ copper} = \dfrac{1.11}{1.39} \times 100$

$= 79.5\%$

Sample B:  $\% \text{ copper} = \dfrac{1.15}{1.43} \times 100$

$= 80\%$

Sample C:  $\% \text{ copper} = \dfrac{1.20}{1.51} \times 100$

$= 79.5\%$

This indicates that, within experimental error, the oxide of copper has a fixed copper: oxygen ratio.

Proust's ideas did not find immediate acceptance. In particular, another French chemist Berthollet put forward arguments against the law. Proust showed by experiment that the examples, quoted by Berthollet to contradict the law, were in fact mixtures of two or more compounds. In order to make it clear just exactly what substances are covered by the law of constant composition, it is now stated as:

*All pure samples of the same chemical compound, however prepared, contain the same elements in the same ratio by mass.*

This law is sometimes known as the law of definite (or fixed) proportion.

These two laws of chemical combination are observed facts, but the scientist tries to go beyond the facts to the consideration of an explanation. He may make a guess about the explanation. Such a guess is called a *hypothesis*. If the hypothesis fits the observed facts and is capable of predicting further observations which are then made in accordance with the prediction, then the hypothesis is generally known as a *theory*. As long as the theory works as an explanation, it is acceptable. If new facts come to light which cannot be explained, the theory has to be modified or discarded. At the beginning of the nineteenth century John Dalton proposed the Atomic Theory as an explanation of the laws of chemical combination. Since then, science has developed into a major human activity. Discovery has followed discovery and it might well be thought that the atomic theory had outlived its usefulness. In the next volume of this Chemistry course you will learn how it is now necessary to modify some of the atomic theory, but the idea remains unscathed. In the nineteenth century there would have been little development of chemistry without it, and today it still has value in its application to most of the problems met in the laboratory and in industry.

## 3. Dalton's Atomic Theory

It is interesting to trace the origins of Dalton's Atomic Theory, but space forbids this and only a few general points can be made. The idea that matter consists of very small indivisible particles called atoms is very old. In ancient times this was especially taught by the Greek philosophers Leukippos and Demokritus (about 450–400 B.C.). In a work attributed to Kanada (about 500 B.C.) the atomic theory occurs, and this is developed in Buddhist and Jain writings from the second century B.C. After this time interest in the atomic theory lapsed, only to be revived in the seventeenth century. Newton, in particular, made use of the atomic theory. He worked out Boyle's Law by assuming that a gas was composed of particles capable of repelling each other. It was through an interest in gases that Dalton himself was led to the atomic theory. The properties which Dalton gave to atoms were necessary because of the behaviour of matter. Mass is not destroyed, so atoms must be indestructible. Since things combine together in simple ratios, atoms must also have the capacity for combining in simple ratios. In one of Dalton's notebooks the following entry, dated 1803, occurs:

'A train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination with one another.' This brings out Dalton's most important contribution — giving atoms the property of weight (mass is the term which we use today). Dalton's Atomic Theory can be summarized as follows:

(i) Matter is made up of minute indivisible particles called atoms.

(ii) Every atom has a definite weight.

(iii) Different elements have atoms differing in weight.

(iv) Atoms combine to form compounds in definite ratios of whole numbers, usually small.

There was general acceptance of Dalton's theory, although some disagreement persisted even into this century. The application of Dalton's ideas was not as simple as the ideas themselves. Some sixty years of trial and error were required in order to find the ratios in which atoms combine, and then the relative weights of the atoms. There is no point in tracing the developments of those years, since the weights of atoms can be determined relatively simply now (see Chapter 18). The ratios in which the atoms combine are now obtained from a more detailed knowledge of the atom itself. To help you to write down the formulas of compounds such as those already given, the simple results of this knowledge are given.

## 4. Valency

Listed below are the formulas of some compounds of hydrogen:

| | |
|---|---|
| Hydrogen chloride | $HCl$ |
| Water | $H_2O$ |
| Ammonia | $NH_3$ |
| Methane | $CH_4$ |

Here we see that different elements have different powers of combining with hydrogen. The *combining power* of an atom is also called its *valency*. Valency is a property of an atom, which will be investigated later. At this stage, valency is to be regarded simply as a number, the use of which helps in the writing of formulas. As a number, valency is defined as:

*The valency of an element is the number of hydrogen atoms which will combine with or displace one atom of the element.*

Applying this to the list above, chlorine in hydrogen chloride has a valency of 1, oxygen a valency of 2, nitrogen 3, and carbon 4. A table of common valencies is given below.

| Valency 1 (monovalent) | Valency 2 (divalent) | Valency 3 (trivalent) | Valency 4 (tetravalent) |
|---|---|---|---|
| Potassium | Calcium | Aluminium | Carbon |
| Sodium | Copper (II) — cupric | Iron (III) — ferric | Lead (IV) — plumbic |
| Copper (I) — cuprous | Iron (II) — ferrous | Nitrogen | |
| Chlorine — chloride | Lead (II) — plumbous | | |
| | Magnesium | | |
| | Mercury (II) — mercuric | | |
| | Zinc | | |
| | Sulphur — sulphide | | |
| | Oxygen — oxide | | |

From this table it is immediately apparent that some elements have more than one valency. It is not difficult to know which valency to use if the Roman numeral is written after the name of the element. Thus copper (I) refers to copper having valency of 1, mercury (II) means mercury with a valency of 2, iron (III) is iron with a valency of 3 and so on. In older books you will come across names like cuprous, mercuric, ferric standing for the different valencies. There is a general rule that the ending '-ous' stands for the lower valency and '-ic' for the higher one. But, for example, '-ic' represents a valency of 2 for copper, 3 for iron and 4 for lead. In addition some elements have more than two valencies so that yet another word ending is required.

## 5. Rules for writing formulas

The table of valencies should be learned and then applied to writing formulas according to the rules given below. A word of warning — the fact that a formula can be written does not mean that such a compound exists. Copper and hydrogen might, for example, be thought to form copper hydride $CuH_2$, but such a compound does not, in fact, exist.

The first rule to note is that if two elements have the same valency, then

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a molecule of the compound formed between them will be represented by a formula containing one atom of each element. For example,

| | |
|---|---|
| Potassium chloride | KCl |
| Calcium oxide | CaO |
| Iron (II) sulphide | FeS |
| Aluminium nitride | AlN |

The reason for this is that the combining power of an atom is satisfied if it combines with another of the same combining power. The compounds listed above are formed by a metal and a non-metal — the name of the metal being written first and the non-metal taking the ending '-ide'. In making use of the table of valencies, it would be best at this stage to practise with compounds formed between a metal and a non-metal.

When the valencies of the elements are different, the first step is to note the lowest common multiple (LCM) of the two valencies. For example, *Aluminium oxide:* aluminium valency 3, oxygen valency 2, gives LCM = 6. It has already been seen that the number of atoms of each element in a molecule is represented by a subscript, so the next step is to determine the subscript. This is done by dividing the LCM by each valency. Thus in the example given,

for aluminium $6/3 = 2$ and for oxygen $6/2 = 3$. Therefore the formula for aluminium oxide is written as: $Al_2O_3$.

Further examples of the application of this rule are:

(i) *Sodium oxide:* sodium valency 1, oxygen valency 2. LCM = 2.

For sodium $2/1 = 2$, for oxygen $2/2 = 1$.
∴. The formula of sodium oxide can be written as $Na_2O$

(ii) *Magnesium chloride:* magnesium valency 2, chlorine valency 1. LCM = 2.

For magnesium $2/2 = 1$, for chlorine $2/1 = 2$
∴. The formula of magnesium chloride is $MgCl_2$

(iii) *Calcium nitride:* calcium valency 2, nitrogen valency 3. LCM = 6.

For calcium $6/2 = 3$, for nitrogen $6/3 = 2$
∴. The formula of calcium nitride is $Ca_3N_2$

(iv) *Lead (IV) oxide:* lead (IV) valency 4, oxygen valency 2. LCM = 4.

For lead (IV) $4/4 = 1$, for oxygen $4/2 = 2$
∴. The formula of lead (IV) oxide is $PbO_2$.

The simple compounds formed between non-metals and hydrogen can be written down at once. This is because the definition of valency is the number of hydrogen atoms with which one atom of the element will combine. So, sulphur with a valency of 2 gives the hydride written as $H_2S$ and usually called hydrogen sulphide. Nitrogen valency 3 gives the hydride $NH_3$ — ammonia. This formula and those of other hydrides were given at the beginning of this section to introduce the idea of valency.

The valency rules already given could be used to give the formulas of some compounds formed between non-metals; e.g.

(i) *Carbon chloride:* carbon valency 4, chlorine valency 1. LCM = 4.

    For carbon $4/4 = 1$, for chlorine $4/1 = 4$.

    ∴ the formula of carbon chloride is $CCl_4$.

(N.B. to show the four chlorine atoms in this formula, the compound is named carbon *tetra*chloride.)

(ii) *Carbon oxide:* carbon valency 4, oxygen valency 2. LCM = 4.

    For carbon $4/4 = 1$, for oxygen $4/2 = 2$.

    ∴ the formula of carbon oxide is $CO_2$ — this is the formula of the compound better known as carbon *dioxide*.

In most cases, the valency rules do not help in writing the formulas of compounds formed between non-metals. For example, compounds of nitrogen and oxygen with formulas $N_2O$, $NO$ and $NO_2$ have already been encountered. These formulas will have to be learned. Even at an advanced level there is no simple pattern to explain the formation of these different oxides of nitrogen. However, it must be emphasised that they do exist and that their formulas can be determined by methods given in the next chapter.

## 6. Radicals and their valencies

In earlier work, you will have noticed that in many compounds, all having part of their name in common, there is a common group of atoms. For example, all carbonates contain the group $CO_3$, all ammonium compounds have the group $NH_4$ and all nitrates the group $NO_3$. A group of atoms which behaves as a single unit in compounds is known as a *radical*.

*A radical is a group of atoms which behaves as a single unit in a number of compounds.*

Consider the following compounds:

| | |
|---|---|
| Sodium sulphate | $Na_2SO_4$ |
| Copper sulphate | $CuSO_4$ |
| Iron (III) sulphate | $Fe_2(SO_4)_3$ |
| Sulphuric acid | $H_2SO_4$ |

It is apparent that the radical, in this case the sulphate radical $SO_4$, has its own particular combining power or valency. In sulphuric acid, the radical has a valency of 2. A table showing the valencies of the common radicals is given below:

| Valency 1 | | Valency 2 | |
|---|---|---|---|
| Ammonium | $NH_4$ | Carbonate | $CO_3$ |
| Hydroxide | OH | Sulphate | $SO_4$ |
| Nitrate | $NO_3$ | Sulphite | $SO_3$ |
| Hydrogencarbonate | | | |
| (bicarbonate) | $HCO_3$ | | |
| Hydrogensulphate | | | |
| (bisulphate) | $HSO_4$ | | |

## 7. Formulas involving radicals

In order to write formulas in which radicals occur, it must first be emphasized that radicals are to be regarded as single units whose composition does not vary. So, if the formula requires more than one radical, it must be contained in brackets with the relevant subscript written outside e.g. $(OH)_3$, $(NO_3)_2$, $(NH_4)_2$. Formulas involving radicals are found by applying the rules as before. The following examples are given in which both parts of the compound have the same valency:

| | |
|---|---|
| Sodium hydroxide | $NaOH$ |
| Potassium nitrate | $KNO_3$ |
| Ammonium chloride | $NH_4Cl$ |
| Lead (II) carbonate | $PbCO_3$ |
| Magnesium sulphate | $MgSO_4$ |

Using the rule for different valencies, some examples are given below:

(i) *Potassium sulphate:* potassium valency 1, sulphate valency 2.

LCM = 2. For potassium $2/1 = 2$, for sulphate $2/2 = 1$.

∴ the formula for potassium sulphate is $K_2SO_4$.

(ii) *Calcium hydrogencarbonate:* calcium valency 2, hydrogencarbonate valency 1. LCM = 2.

For calcium $2/2 = 1$, for hydrogencarbonate $2/1 = 2$

∴ the formula for calcium hydrogencarbonate is $Ca(HCO_3)_2$.

(iii) *Aluminium hydroxide:* aluminium valency 3, hydroxide valency 1.

LCM = 3. For aluminium $3/3 = 1$, for hydroxide $3/1 = 3$

∴ the formula for aluminium hydroxide is $Al(OH)_3$.

(iv) *Ammonium carbonate:* ammonium valency 1, carbonate valency 2.

LCM = 2. For ammonium $2/1 = 2$, for carbonate $2/2 = 1$

∴ the formula for ammonium carbonate is $(NH_4)_2CO_3$.

(v) *Lead (II) nitrate:* lead (II) valency 2, nitrate valency 1. LCM = 2.

For lead $2/2 = 1$, for nitrate $2/1 = 2$

∴ the formula for lead (II) nitrate is $Pb(NO_3)_2$.

(vi) *Iron (III) sulphate:* iron (III) valency 3, sulphate valency 2. LCM = 6.

For iron $6/3 = 2$, for sulphate $6/2 = 3$

∴ the formula for iron (III) sulphate is $Fe_2(SO_4)_3$.

All the formulas worked out in this chapter can be shown to be correct by experiment. In fact, the practical determination of the composition of compounds is the basis for the rules which have been given. There is no necessity to repeat this practical work because the formulas of simple compounds, particularly those formed between metals and non-metals, can be deduced from a knowledge of the valencies of the combining entities. In the next chapter, some examples of the deduction of formulas from experimental results will be given.

## Questions

1 State the Law of Conservation of Mass. Describe briefly an experiment you would perform to show the truth of this law in a reaction in which burning takes place.

2 A flask containing a solution of barium chloride weighed 140.0 g. A small test-tube containing dilute sulphuric acid weighed 28.2 g. The tube was carefully lowered into the flask, which was then stoppered with a cork weighing 0.2 g. The stoppered flask and contents were then weighed. The two chemicals were then mixed, and the flask and contents were re-weighed.

   a What is the total mass of the stoppered flask and contents before mixing and after mixing?

   b What do you see when the two chemicals are mixed?

   c Write a word equation for the chemical change which takes place.

   d Do you consider that this experiment proves the Law of Conservation of Mass? Explain your answer.

3 State the Law of Constant Composition.
   Starting from metallic copper, outline the method by which you could obtain: (a) a solution of copper nitrate, (b) copper hydroxide. State how, from each of these products, it is possible to obtain copper oxide. How would you use these two samples of copper oxide to demonstrate the law you have stated?

4 Analysis of two different samples of metal oxides gave the following results:

| Sample | Weight of metal oxide | Weight of metal |
|---|---|---|
| A | 5.36 g | 4.97 g |
| B | 4.98 g | 4.662 g |

Show that these figures support the Law of Constant Composition.

5 If 18 g of magnesium combine with 12 g of oxygen to form magnesium oxide, what mass of magnesium oxide could be formed from 3.6 g of magnesium?

6 Write down the formulas of the (i) oxides, (ii) chlorides, (iii) sulphides and (iv) nitrides of the following:

   (a) sodium, (b) magnesium and (c) aluminium.

7 Write down the formulas for the (i) hydroxides and (ii) sulphates of the following:

   (a) iron (III), (b) copper (II), (c) ammonium.

8 Write down the formulas for ammonium chloride and ammonium nitrate.

**9** Give the formulas of the following substances:

sodium sulphite, potassium hydrogensulphate, zinc sulphide, carbon disulphide, calcium chloride and calcium hydride.

**10** A metallic element, M, has valencies 2 and 3. Write down the formulas for its oxides, chlorides, carbonates, nitrates, phosphates ($PO_4$ — valency 3), and hydroxides.

# 18
# Some Fundamental Calculations

DALTON's particular contribution to atomic theory was to give atoms the property of weight. Dalton said that the weight of an atom was the same for all the atoms of a particular element and different from those of the atoms of other elements. It was realised, as soon as Dalton proposed his ideas, that the determination of the weights of atoms would have important results. Knowing the relationship between the weights of different atoms which react with one another, the chemist is able to predict the quantities of material which will be involved in chemical reactions. This is the basis of the controlled production of iron and steel, of plastics, of medicines, of vanaspati, of fertilizers, and of an endless list of manufactured goods.

## 1. Atomic weight

Dalton was not concerned with the actual weight of an atom. He and those following him saw that it was sufficient to know the relative weights of atoms. The relative weight of an atom of an element is called the *atomic weight* of the element. It is the weight of one atom of an element compared with the weight of one atom of the chosen standard element. The comparison of the two weights gives a *number* which stands for the number of times one atom of the element is heavier than the standard.

Originally the standard was the weight of the hydrogen atom. This was chosen because hydrogen, being the lightest known element, was supposed to have the lightest atoms. On this standard, the weights of all other atoms were greater than 1. For example, the atomic weight of oxygen is 15.88, that is, one atom of oxygen is 15.88 times heavier than one atom of hydrogen.

The hydrogen standard was limited in its use because hydrogen did not form compounds with many elements. Atomic weights were experimentally determined from compounds formed with oxygen. So it was reasonable to change to oxygen as a standard. Clearly to assign the value of 1 to the oxygen atom would give fractional values to the atomic weights of elements lighter than oxygen. To avoid this the atomic weight of oxygen is taken as 16 (This is written shortly as $O = 16.000$). The carbon atom is 3/4 as heavy as an oxygen atom so the atomic weight of carbon is 12 ($C = 12$). The sulphur atom is twice as heavy as an oxygen atom, so $S = 32$.

## 2. Experimental determination of atomic weight: the carbon standard

Since 1961, a single international standard has been in use. The reason for the change is connected with the way in which atomic weights are now determined. The weights of atoms are compared without any need to carry out chemical reactions. An instrument called a *mass spectrometer* is used.
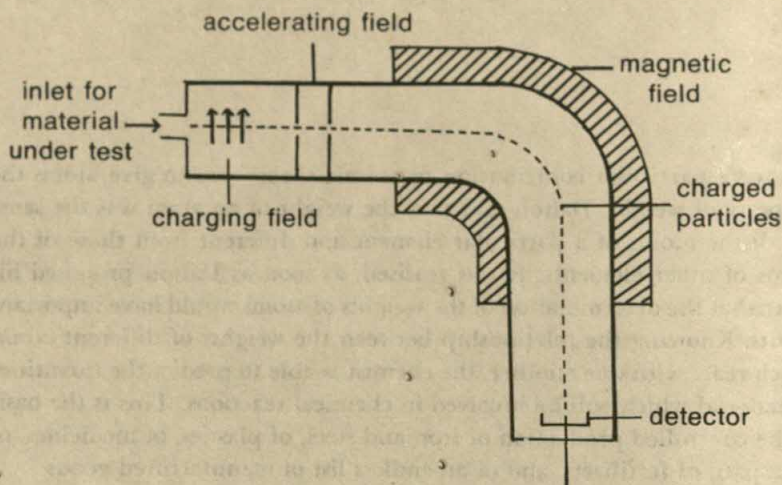


Fig. 18.1  **Mass Spectrometer**

The material to be tested gains an electric charge as it enters the instrument. All the charged particles are accelerated to the same speed before entering a very strong magnetic field. The magnetic field causes the charged particles to change direction. Using pure carbon as the starting material, the magnetic field is adjusted until the charged carbon atoms are deflected on to the detector. The value of this magnetic field is noted and then other elements are put into the system. Atoms of elements lighter than carbon will require a weaker field to deflect them to the same extent i.e. on to the detector; atoms of heavier elements will require a stronger field. So the (relative) atomic weights of elements can be determined. The atomic weight of carbon using the carbon standard is taken as 12, i.e. C = 12.000. This leads to the following definition of atomic weight:

*The atomic weight of an element is the ratio of the mass of one atom of the element to 1/12 of the mass of an atom of carbon-12 ($^{12}C$ = 12.000).*

Atomic weight of an element = mass of 1 atom of the element

$$: \frac{1}{12} \times \text{mass of 1 atom of carbon-12}$$

$$= \frac{\text{mass of 1 atom of the element}}{\text{mass of 1 atom of carbon-12}} \times 12$$

The symbol $^{12}C$ stands for those atoms of carbon which are the smallest particles of carbon-12. From this you will gather that all atoms of the same element are not identical in weight. The full implications of this will be gone into later. For the present it is enough to know that carbon-12 is the name given to carbon composed only of the commonest carbon atoms.

## 3. Molecular weight

Molecules are made up of atoms and so the addition of the weights of the atoms present will give the weight of the molecule. The molecular weight could also be determined by the mass spectrometer and is therefore defined as follows:

*The molecular weight of a compound is the ratio of the mass of one molecule of the compound to 1/12 of the mass of an atom of carbon-12.*

## 4. Atomic weights of some common elements

In both the above definitions the word 'mass' has been used. This is because they are definitions and the common word 'weight' has another special meaning. As a result, strict terminology demands the use of the term *relative atomic mass* for what is commonly known as atomic weight. In this series of books, the term 'atomic weight' will continue to be used because it is the common usage. A table of approximate atomic weights is given below.

| Aluminium | 27 | Hydrogen | 1 | Oxygen | 16 |
|---|---|---|---|---|---|
| Argon | 40 | Iodine | 127 | Phosphorus | 31 |
| Barium | 137 | Iron | 56 | Potassium | 39 |
| Bromine | 80 | Lead | 207 | Silver | 108 |
| Calcium | 40 | Magnesium | 24 | Sodium | 23 |
| Carbon | 12 | Manganese | 55 | Sulphur | 32 |
| Chlorine | 35.5 | Mercury | 201 | Tin | 119 |
| Copper | 63.5 | Nitrogen | 14 | Zinc | 65 |

The scientists of today have accomplished what Dalton would have regarded as impossible. The actual weights of atoms have been determined. For example, one hydrogen atom weighs:

$$0.000\ 000\ 000\ 000\ 000\ 000\ 000\ 00167 \text{ g}$$

which can be written as $1.67 \times 10^{-24}$ g, and one atom of oxygen weighs:

$$0.000\ 000\ 000\ 000\ 000\ 000\ 000\ 0266 \text{ g or } 26.6 \times 10^{-24} \text{g.}$$

While these numbers are interesting, they have little practical value. They are only given for the purpose of illustrating how small atoms are and how little they weigh, and should not be memorized.

## 5. The gram-atom and the gram-molecule

The figures for the actual weight of the atoms of hydrogen and oxygen lead to the calculation of the number of atoms in different weights of the element. Consider, for example, 1 g of hydrogen. Using the weight of a hydrogen atom given above, the number of atoms in 1 g of hydrogen works out to about $6 \times 10^{23}$. If the same number of oxygen atoms were taken, they would weigh about 16 g. This is not really surprising since it has already been discovered that one oxygen atom is 16 times heavier than one hydrogen atom. This ratio remains unchanged provided always that the weights of equal numbers of atoms of hydrogen and oxygen are compared. This can be written as follows:

$$\frac{\text{weight of } 6 \times 10^{23} \text{ atoms of hydrogen}}{\text{weight of } 6 \times 10^{23} \text{ atoms of oxygen}} = \frac{\text{weight of 1 atom of hydrogen.}}{\text{weight of 1 atom of oxygen}}$$

It is inconvenient to always have to write $6 \times 10^{23}$, so this number is represented by the symbol $L$. The number is called the *Avogadro constant* or *Avogadro number*. If this number of particles of any kind of matter is taken, then the quantity of matter involved is called the *mole*. Thus a mole of hydrogen atoms weighs 1 g; a mole of oxygen atoms weighs 16 g. This is simply the atomic weight expressed in grams, and in this context the mole would be referred to as a *gram-atom* (g-atom). If $6 \times 10^{23}$ molecules were involved, the weight of substance would then be the molecular weight expressed in grams, which is called one *gram-molecule* of the substance.

## 6. The empirical formula of a compound

The gram-atom is useful when it comes to working out the formulas of compounds from experimental results. Consider the analysis of copper oxide given in the previous chapter. The results show that the oxide is 80% copper and 20% oxygen. Thus in 100 g of oxide:

80 g of copper is combined with 20 g of oxygen.
1 g-atom of copper weighs 63.5 g
and 1 g-atom of oxygen weighs 16 g

$$\therefore 80 \text{ g of copper} = \frac{80}{63.5} \text{ g-atom of copper}$$
$$= 1.26 \text{ g-atom of copper}$$

$$\text{and } 20 \text{ g of oxygen} = \frac{20}{16} \text{ g-atom of oxygen}$$
$$= 1.25 \text{ g-atom of oxygen.}$$

$\therefore$ 1.26 g-atom of copper is combined with 1.25 g-atom of oxygen.

This ratio in g-atoms is 1:1 (the slight difference being attributed to experimental error).

i.e. 1 g-atom of copper combines with 1 g-atom of oxygen
$\therefore L$ atoms of copper are combined with $L$ atoms of oxygen
i.e. 1 atom of copper is combined with 1 atom of oxygen.

This simple ratio of the numbers of atoms of each element in a compound obtained by experiment, is known as the *empirical formula* of the com-

pound. So, the empirical formula of copper oxide is CuO. (Compare this with the formula of copper (II) oxide written according to the valency rules).

## 7. Numerical calculation of empirical formula

In the calculation of the empirical formula of copper oxide, the same numerical result would have been obtained, if the weights of the two elements had been divided simply by the atomic weights. The result could be expressed as a ratio of atoms. For example:

(i) 2.89 g of lead combine with 0.45 g of sulphur.

|  | Lead |  | Sulphur |
|---|---|---|---|
| Ratio by weight | 2.89 | : | 0.45 |
| Ratio by atoms | $\dfrac{2.89}{207}$ | : | $\dfrac{0.45}{32}$ |
| i.e. | 0.0140 | : | 0.0141 |
| or | 1 | : | 1 |

∴ the empirical formula of lead sulphide is PbS.

(ii) A compound contains 40% of calcium, 12% of carbon and 48% of oxygen.

|  | Calcium |  | Carbon |  | Oxygen |
|---|---|---|---|---|---|
| Ratio by weight | 40 | : | 12 | : | 48 |
| Ratio by atoms | $\dfrac{40}{40}$ | : | $\dfrac{12}{12}$ | : | $\dfrac{48}{16}$ |
| or | 1 | : | 1 | : | 3 |

∴ the empirical formula of the compound is $CaCO_3$.

(iii) Analysis of a compound shows it to contain 4.34 g of sodium, 1.13 g of carbon and 4.53 g of oxygen.

|  | Sodium |  | Carbon |  | Oxygen |
|---|---|---|---|---|---|
| Ratio by weight | 4.34 | : | 1.13 | : | 4.53 |
| Ratio by atoms | $\dfrac{4.34}{23}$ | : | $\dfrac{1.13}{12}$ | : | $\dfrac{4.53}{16}$ |
| i.e. | 0.189 | : | 0.094 | : | 0.283 |
| Dividing by the lowest value to get the simplest whole number ratio. | $\dfrac{0.189}{0.094}$ | : | $\dfrac{0.094}{0.094}$ | : | $\dfrac{0.283}{0.094}$ |
| or | 2 | : | 1 | : | 3 |

∴ the empirical formula of the compound is $Na_2CO_3$.

(iv) A compound contains 0.52 g of potassium, 0.64 g of oxygen, and 0.47 g of chlorine.

|  | Potassium |  | Oxygen |  | Chlorine |
|---|---|---|---|---|---|
| Ratio by weight | 0.52 | : | 0.64 | : | 0.47 |
| Ratio by atoms | $\dfrac{0.52}{39}$ | : | $\dfrac{0.64}{16}$ | : | $\dfrac{0.47}{35.5}$ |
| i.e. | 0.013 | : | 0.04 | : | 0.013 |

Dividing by the least value
0.013 we get                1  :  3  :  1

∴ the empirical formula of the compound is KO₃Cl.

This is normally written KClO₃.

## 8. Numerical calculation of molecular weight

Earlier in this chapter it was said that the molecular weight of a compound could be determined by adding together the atomic weights of the elements making up one molecule of the compound. Some examples of this are given below:

(i) The molecular weight of sodium hydrogencarbonate $NaHCO_3$.

$$Na \quad H \quad C \quad O_3$$
$$23 + 1 + 12 + 3 \times 16$$
$$= 23 + 1 + 12 + 48$$
$$= 84.$$

(ii) The molecular weight of nitric acid $HNO_3$.

$$H \quad N, \quad O_3$$
$$1 + 14 + 3 \times 16$$
$$= 1 + 14 + 48$$
$$= 63.$$

(iii) The molecular weight of calcium hydroxide $Ca(OH)_2$.
For this calculation the formula is more conveniently written as $CaO_2H_2$.

$$Ca \quad O_2 \quad H_2$$
$$40 + 2 \times 16 + 2 \times 1$$
$$= 40 + 32 + 2$$
$$= 74.$$

(iv) The molecular weight of aluminium sulphate $Al_2(SO_4)_3$
i.e. $Al_2S_3O_{12}$.

$$Al_2 \quad S_3 \quad O_{12}$$
$$2 \times 27 + 3 \times 32 + 12 \times 16$$
$$= 54 + 96 + 192$$
$$= 342.$$

## 9. The percentage composition of a compound

Following the determination of molecular weights, the percentage compositions of the compounds can be calculated. That is, the percentage of each element present in the compound is worked out. Consider the compounds whose molecular weights have been determined above:

(i) Percentage composition of sodium hydrogencarbonate:

$$\% \text{ Sodium} = \frac{23}{84} \times 100 = 27.4$$

$$\% \text{ Hydrogen} = \frac{1}{84} \times 100 = 1.2$$

$$\% \text{ Carbon} = \frac{12}{84} \times 100 = 14.3$$

$$\% \text{ Oxygen} = \frac{48}{84} \times 100 = 57.1$$

$$\overline{100.0\%}$$

Calculating all the percentages and adding them up provides a check on the calculation.

(ii) Percentage composition of nitric acid:

$$\% \text{ Hydrogen} = \frac{1}{63} \times 100 = 1.6$$

$$\% \text{ Nitrogen} = \frac{14}{63} \times 100 = 22.3$$

$$\% \text{ Oxygen} = \frac{48}{63} \times 100 = 76.1$$

(iii) Percentage composition of calcium hydroxide:

$$\% \text{ Calcium} = \frac{40}{74} \times 100 = 54$$

$$\% \text{ Oxygen} = \frac{32}{74} \times 100 = 43.3$$

$$\% \text{ Hydrogen} = \frac{2}{74} \times 100 = 2.7$$

(iv) Percentage composition of aluminium sulphate:

$$\% \text{ Aluminium} = \frac{54}{342} \times 100 = 15.8$$

$$\% \text{ Sulphur} = \frac{96}{342} \times 100 = 28.1$$

$$\% \text{ Oxygen} = \frac{192}{342} \times 100 = 56.1$$

These calculations can be extended in the following way:

(i) Calculate the weight of oxygen in 50 g of mercury (II) oxide

The formula of mercury (II) oxide is HgO.

Thus 1 g-molecule of mercury (II) oxide contains 1 g-atom of oxygen

The g-molecule of mercury (II) oxide is $201 + 16 = 217$ g

$\therefore$ 217 g of mercury (II) oxide contain 16 g of oxygen

So 50 g of mercury (II) oxide contain $\frac{16}{217} \times 50$ g of oxygen

$$= 3.69 \text{ g}.$$

This calculation shows the weight of oxygen which could be obtained by heating 50 g of mercury (II) oxide.

(ii) Calculate the weight of water of crystallization in 20 g copper sulphate–5–water ($CuSO_4.5H_2O$).

The molecular weight of $CuSO_4.5H_2O$ is:

$$
\begin{array}{ccccccc}
Cu & S & O_4 & & H_{10} & & O_5 \\
63.5 & + 32 & + 4 \times 16 & + & (10 \times 1 & + & 5 \times 16) \\
= 63.5 & + 32 & + 64 & + & (10 & + & 80) \\
\end{array}
$$
$$= 249.5.$$

In 1 g-molecule of copper sulphate–5–water there are 5 g-molecules of water i.e. 249.5 g of solid contain 90 g of water.

$$\text{In 20 g of solid there are } \frac{90}{249.5} \times 20 \text{ g of water}$$

$$= 7.22 \text{ g of water.}$$

Thus if 20 g of copper sulphate–5–water were heated to give the anhydrous salt, 7.22 g water would be obtained..

## 10. Writing correct equations

Chemical change results in the formation of new substances and this has been shown by writing a word equation. The word equation helps to explain what substances are used and what products are formed. Underneath the word equation the chemical equation was written, and we are now going to study these in order to learn how they can be written.

Hydrogen burns in oxygen to produce water. This is an experimental fact and comes before the writing of the equation. To write the equation, the symbols and formulas of all the *reactants* are put on the left hand side and those of the *products* on the right hand side. If more than one substance appears on either side of the equation, a + sign connects them. An arrow ⟶ separates the left from the right side of the equation. The arrow can be read as 'produces', 'gives', 'forms' and 'yields'. It shows that the reactants on the left give the products on the right. Applying all this to the reaction between hydrogen and oxygen, we can write to begin with:

$$H_2 + O_2 \longrightarrow H_2O$$

This brings out the need to write correct formulas. For hydrogen and oxygen the correct formulas are $H_2$ and $O_2$ because these gases are made up of diatomic molecules. From the valency rules, $H_2O$ is correct for water.

Not only must an equation represent the facts and have the correct formulas, it must have the same number of atoms of each kind on each side of the equation. This is consistent with the Law of Conservation of Mass. With the equation $H_2 + O_2 \longrightarrow H_2O$, the number of oxygen atoms is not balanced. The balancing of an equation is simply a matter of counting the atoms of each kind on each side of the equation, followed by adjusting the number of molecules to give the required number of atoms. A correctly written formula must not be changed. Thus in $H_2 + O_2 \longrightarrow H_2O$, a

simple balance could be obtained by writing $H_2 + O \longrightarrow H_2O$. But, O is not the correct formula for oxygen gas. To write the correct equation in this case requires two more steps:

(1) Put $2H_2O$ on the right hand side.

$$H_2 + O_2 \longrightarrow 2H_2O$$
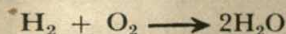
This balances the oxygen, but the right hand side now has 4 hydrogen atoms, so:

(2) Write $2H_2$ on the left hand side

$$2H_2 + O_2 \longrightarrow 2H_2O.$$
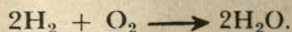
The equation is now balanced.

From this detailed discussion on the writing of a particular equation, the following rules emerge:

(1) The equation must represent facts.

(2) The symbols and formulas of all reactants and products must be correctly written. Special attention should be given to the atomicities of the elements.

(3) There must be the same number of atoms of each kind on each side of the equation.

These rules are now applied to some other substances:

(i) The action of heat on mercury (II) oxide decomposes it into mercury and oxygen.

$$HgO \longrightarrow Hg + O_2 \uparrow$$

Balancing O atoms: $\quad 2HgO \longrightarrow Hg + O_2 \uparrow$

Balancing Hg atoms: $\quad 2HgO \longrightarrow 2Hg + O_2 \uparrow$
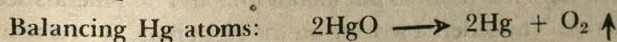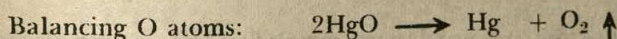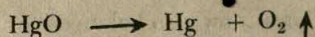
(ii) When dilute hydrochloric acid is added to calcium carbonate, carbon dioxide is liberated, and calcium chloride and water are also formed.

$$CaCO_3 + HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$
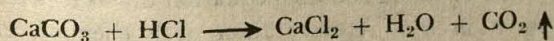
This equation is balanced simply by writing $2HCl$.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \uparrow$$
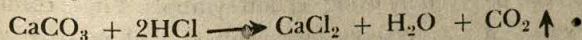
(iii) Zinc reacts with dilute hydrochloric acid to liberate hydrogen and form zinc chloride.

$$Zn + HCl \longrightarrow ZnCl_2 + H_2 \uparrow$$

Balancing H atoms: $Zn + 2HCl \longrightarrow ZnCl_2 + H_2 \uparrow$
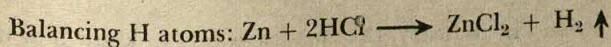
This also results in the balancing of the Cl atoms.

(iv) Lead nitrate when heated decomposes into lead oxide, nitrogen dioxide and oxygen.

$$Pb(NO_3)_2 \longrightarrow PbO + NO_2 \uparrow + O_2 \uparrow$$
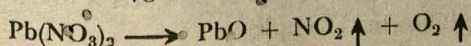
As written, Pb atoms are balanced, but neither N or O atoms are balanced.

If 2PbO is written, then O atoms are balanced

$$Pb(NO_3)_2 \longrightarrow 2PbO + NO_2 \uparrow + O_2 \uparrow$$
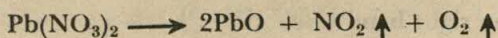
The Pb atoms must now be adjusted:

$$Pb(NO_3)_2 \longrightarrow 2PbO + NO_2 \uparrow + O_2 \uparrow$$
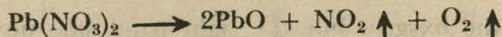
Now try balancing the N atoms; this can be done by writing 4NO$_2$

$$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 \uparrow + O_2 \uparrow$$
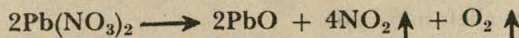
Everything else now balances.

(v) Mixing solutions of aluminium sulphate and calcium hydroxide results in a precipitate of aluminium hydroxide and calcium sulphate.

$$Al_2(SO_4)_3 + Ca(OH)_2 \longrightarrow Al(OH)_3 \downarrow + CaSO_4 \downarrow$$

The radicals are only exchanged and so it is convenient to treat them as single units.

Starting with Al atoms, the equation can be written as:

$$Al_2(SO_4)_3 + Ca(OH)_2 \longrightarrow 2Al(OH)_3 \downarrow + CaSO_4 \downarrow$$

Next, sulphate radicals can be adjusted:

$$Al_2(SO_4)_3 + Ca(OH)_2 \longrightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 \downarrow$$

Adjusting Ca atoms:

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 \downarrow + 3CaSO_4 \downarrow$$

The equation is now also balanced for OH radicals.

In writing equations, it is usual to put metals first and non-metals second on the left hand side. The order of writing on the right hand side is usually: solids, liquids and substances in solution and finally gases.

Note that strictly the use of the word 'balanced' for an equation is unnecessary. A chemical equation is not an equation unless it is balanced.

The chemical equation is a representation of a chemical reaction showing the symbols and formulas of the reactants and products. Additional information can be given by using certain symbols. Those commonly used are an arrow upwards $\uparrow$ to show a gas evolved, and an arrow downwards $\downarrow$ to show a solid precipitated. Other symbols will be introduced in the appropriate places as required.

## 11. Practical information from chemical equations

In the laboratory and in industry, the chemist wants to know how much of the reacting substances he must put together and how much of each product he can expect. This is the most useful information which can be obtained from a chemical equation. The arithmetic involved in these calculations of reacting weights and weights of products is straightforward and is illustrated by the following examples:

(i) Calculate the weight of calcium oxide obtained by heating 100 g of calcium carbonate.

Equation: $CaCO_3 \longrightarrow CaO + CO_2$
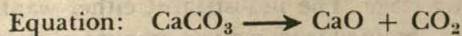
This indicates that 1 molecule of calcium carbonate decomposes to give 1 molecule of calcium oxide and 1 molecule of carbon dioxide (this last bit of information is not required for the calculation). The next step is to write down the molecular weights:

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$(40 + 12 + 3 \times 16) \quad (40 + 16)$$
$$100 \longrightarrow 56$$
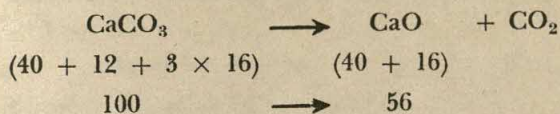
Molecular weights are relative and can therefore be expressed in any units. So, using grams, the equation indicates that 100 g of calcium carbonate gives 56 g of calcium oxide.

(ii) Calculate the weight of calcium carbonate which must be heated in order to make 7 tonnes of calcium oxide.

Using the information from (i) above:

56 tonnes of calcium oxide are formed from 100 tonnes of calcium carbonate

$\therefore$ 7 tonnes of calcium oxide are formed from $\dfrac{100}{56} \times 7$ tonnes

$= 12.5$ tonnes of calcium carbonate.

(iii) Given 200 kg of calcium oxide, how many kilograms of calcium hydroxide can be formed by adding enough water to convert it all into calcium hydroxide?

$$CaO + H_2O \longrightarrow Ca(OH)_2$$
$$(40 + 16) \qquad (40 + 2 \times 16 + 2 \times 1)$$
$$56 \longrightarrow 74$$
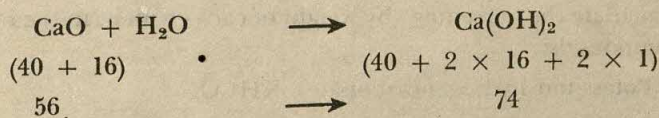
i.e. 56 kg of calcium oxide $\longrightarrow$ 74 kg of calcium hydroxide

$\therefore$ 200 kg of calcium oxide $\longrightarrow \dfrac{74}{56} \times 200$ kg of calcium hydroxide

$= 264.3$ kg of calcium hydroxide.

(iv) If we need 40 g of oxygen for a laboratory experiment, how many grams of hydrogen peroxide must be decomposed?

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
$$2(2 \times 1 + 2 \times 16) \qquad (2 \times 16)$$
$$68 \longrightarrow 32$$
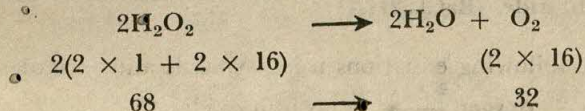
$\therefore$ 40 g of oxygen are formed from $\dfrac{68}{32} \times 40$ g of hydrogen peroxide

$= 85$ g of hydrogen peroxide.

These examples illustrate the basic principles in chemical calculations.

A number of extensions are possible. For example, it is not usual to determine the weight of a gaseous product; instead its volume is calculated. This will be discussed at a later stage. The industrialist either wants to know how much product will be obtained from a given amount of starting material (examples i and iii) or if he needs a certain amount of product, he has to calculate the required amount of starting material (examples ii and iv). This information leads to controlled industrial production as was stated at the beginning of this chapter.

## Questions

(The atomic weights required for the calculations can be found on page 147).

1 Calculate the empirical formulas of compounds of the following compositions by weight:

  a Mg 25.3%   Cl 74.7%

  b Zn 47.8%   Cl 52.2%

  c Na 39.3%   Cl 60.7%

2 Find the empirical formulas of the following compounds from their compositions by weight:

  a Zn 40.5%   S 19.85%   O 39.65%

  b K 44.8%   S 18.4%   O 36.8%

  c Cu 33.9%   N 14.9%   O 51.2%

3 Calculate the percentage by weight of each element in the following compounds:

  a Potassium hydrogencarbonate   $KHCO_3$

  b Methane   $CH_4$

  c Ammonium sulphate   $(NH_4)_2SO_4$

  d Sodium thiosulphate   $Na_2S_2O_3$

4 Calculate the percentage of water of crystallization in crystals of:

  a Sodium carbonate   $Na_2CO_3.10H_2O$

  b Magnesium sulphate   $MgSO_4.7H_2O$

  c Barium chloride   $BaCl_2.2H_2O$

5 Re-write the following equations using symbols and formulas:

  a Potassium + oxygen $\longrightarrow$ potassium oxide

  b Carbon + oxygen $\longrightarrow$ carbon dioxide

  c Copper + oxygen $\longrightarrow$ copper (II) oxide

  d Zinc + chlorine $\longrightarrow$ zinc chloride

  e Sodium + chlorine $\longrightarrow$ sodium chloride

**6** Re-write the following word equations as chemical equations:

a Calcium hydroxide + hydrochloric acid $\longrightarrow$ calcium chloride + water

b Potassium hydroxide + sulphuric acid $\longrightarrow$ potassium sulphate + water

c Copper sulphate + ammonium carbonate $\longrightarrow$ copper carbonate + ammonium sulphate.

**7** Balance the following equations involving the element X and its compounds:

e.g. Unbalanced equation: $X + O_2 \longrightarrow X_2O_3$

Balanced equation: $4X + 3O_2 \longrightarrow 2X_2O_3$

a $X + Fe_2O_3 \longrightarrow X_2O_3 + Fe$

b $XCl + H_2O \longrightarrow X(OH)_3 + HCl$

c $X_2(SO_4)_3 + Pb(NO_3)_2 \longrightarrow X(NO_3)_3 + PbSO_4$

**8** Calculate the weight of oxygen which would combine with 4 g of magnesium.

**9** Suppose that Priestley once heated 54 g of mercury (II) oxide. What weight of mercury did he produce?

**10** How many grams of zinc are needed to set free 3 g of hydrogen from hydrochloric acid?

**11** 76.5 kg of sodium hydrogencarbonate were heated strongly. What weight of carbon dioxide was obtained? If dilute hydrochloric acid had been used, what weight of carbon dioxide would have been obtained in this case?

Equations: (a) $2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2 \uparrow$

(b) $NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2 \uparrow$

**12** What weight of sulphuric acid, $H_2SO_4$, can be prepared from 50 tonnes of sulphur according to the following overall equation:

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4$$
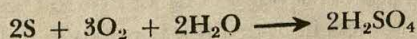
**13** How many kilograms of iron are needed to set free 10 kg of hydrogen from steam?

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2 \uparrow$$

**14** Calculate the weight of calcium hydroxide which on reacting with carbon dioxide gives a precipitate of calcium carbonate weighing 5 g.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

**15** 50 g of ammonium chloride were heated with 40 g of calcium hydroxide. What weight of ammonia gas would be evolved?

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3 \uparrow$$
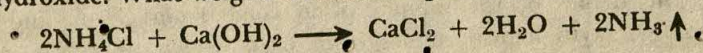
Which of the reagents is in excess and by how much?

# 19
# What's in a Name?

*'What's in a name? that which we call a rose*
*By any other name would smell as sweet.'*

So says Juliet in Shakespeare's well-known play *Romeo and Juliet*. What she says is true and could well be applied to the naming of the chemical elements and their compounds. If ammonia were called nitrogen hydride, it would still turn moist red litmus blue, dissolve readily in water and show all its other properties. However, it would be rather confusing if some chemists used one name and some another. So it is necessary to secure agreement about the name of a substance. The purpose of this chapter is to discuss the names used by chemists, and to give some general rules which are applied to the naming of compounds.

## 1. The names of elements

The naming of elements has been largely a haphazard affair. At the beginning of the seventeenth century, the elements gold, silver, mercury, copper, iron, tin, lead, zinc, arsenic, antimony, bismuth, carbon, and sulphur were known. The origins of these names are obscure because of their long history. It is possible that gold and silver were named because of their colours. The use of the name 'mercury' in English comes from the association of the metal with the planet Mercury. This was first done by the Babylonians, who associated the seven metals known to them with the seven 'planets'. Their seven planets included the Sun (gold) and the Moon (silver). The Greek and Latin name for mercury is more descriptive — 'silver water'. In Latin this is 'hydragyrum' and we get our symbol for mercury from this name 'Hg'. In English, mercury is commonly called 'quicksilver'. The use of a name which describes some property of the element is common. Nearly half the elements are named in this way. For example, chlorine comes from the Greek for 'green', bromine from the Greek for a 'bad smell', and iodine from the Greek for 'violet-colour'.

In naming other elements, the old idea of naming them after planets has been extended. For example, uranium is named after the planet Uranus. The elements which follow it are neptunium and plutonium, just as Neptune and Pluto follow Uranus in their distances from the Sun. Since the names of the planets often come from Greek and Roman mythology, mythological names have been drawn upon directly. The important metal titanium was named in this way by Klaproth in 1801.

Titan was a descendant of Uranus, and titanium was discovered two years after uranium. Klaproth wrote: 'I shall borrow the name for this metallic substance from mythology, as I did in the case of uranium.'

During the nineteenth century there was some attempt to keep to a system in naming the elements. Lavoisier put forward some rules in his book *A Method of Chemical Nomenclature*. In this scheme, the elements already known were to keep their original names. All newly discovered elements were to be recognized as metals or non-metals and given names ending in -*um* if metals, and -*on* if non-metals. This has not worked too well for the non-metals. Only 8 have names ending in '-on', silicon and boron being two examples. Some other non-metals when first discovered were thought to be metals and the names given have not been changed, for example, selenium. Except for the metals known to the ancient world, all others do have names ending in '-ium'.

The Swedish chemist Berzelius was one of the most influential in the naming of elements and, as we have already seen, he was responsible for the use of letters for the symbols of elements. One of his principles for naming elements though, has not been observed. He said 'It is not a good practice to name elements after the places where they have first been found.' In fact, twenty-four elements have been named in this way. Copper is possibly an example of this as the name probably comes from the island of Cyprus from which the ancient world obtained the metal. Other examples are magnesium from Magnesia; californium from California and francium from France.

A further group of elements has been named in honour of a famous person. These are mainly the man-made transuranic elements. For example, einsteinium named after Albert Einstein and curium named after Marie Curie.

The names of the elements vary from one language to another, but their symbols generally form a common language for all chemists. There is one exception. The symbol Az is sometimes used by French chemists for nitrogen. This comes from Lavoisier's name for the element 'azote' meaning 'no life'.

## 2. The names of compounds

Since compounds are formed from elements, it would be helpful if they were named in such a way as to indicate the elements of which they are made. Better still would be a name which indicates just how many atoms of each element are present in the compound. Modern nomenclature, that is the naming of substances, goes a long way towards meeting this ideal. It must be said that the system is not perfect. Consider, for example, the names water, ammonia and methane. These are simple compounds whose composition can be easily remembered, but no clue is given by the name. Water is a compound of hydrogen and oxygen, ammonia a compound of nitrogen and hydrogen and methane a compound of carbon and hydrogen. Ammonia was earlier called 'volatile alkali' or 'alkaline air' (air was used generally to mean gas) and at least these names had the advantage of highlighting a property of the gas. Methane was called 'marsh gas' which indicated where

it could be obtained. On finding out its composition, Dalton called it carburetted hydrogen.

On reading textbooks of Chemistry and the History of Chemistry you will come across many names which have no resemblance to anything you learn now. Some may seem rather fanciful, as for example, 'bile of the serpent' (a compound of calcium and sulphur), 'liver of sulphur' (used to name two different compounds, one being similar to 'bile of the serpent' and the other impure potassium sulphide), and 'salt of eggs' (which was possibly potassium nitrate). Some of the names given to compounds were based on accidental resemblances. 'Butter of antimony' (antimony chloride) looks like butter. 'Oil of vitriol' (concentrated sulphuric acid) looks like olive oil. This name is still occasionally used today along with the following names for salts of sulphuric acid: blue vitriol (copper sulphate–5–water), green vitriol (iron(II) sulphate–7–water) and white vitriol (zinc sulphate–7–water).

Names of other compounds were chosen to show a property of the compound. Caustic soda and caustic potash both burn the skin. These names also help to indicate the source of the compound, caustic soda coming from soda and caustic potash from the ash of plants. We know these compounds as sodium hydroxide and potassium hydroxide respectively. The naming of compounds according to source was fairly common. Of interest in this connection is 'spirit of salt' — the gas we know as hydrogen chloride. This can be obtained from common salt, which in turn is obtained from the sea. When hydrogen chloride dissolves in water it forms an acidic solution which was called 'spirit of sea-water' and then, following Lavoisier's work on acids, it became known as 'muriatic acid' ('mare' is Latin for sea). From muriatic acid another green-coloured gas could be obtained and this was first known as 'oxymuriatic acid' since it was apparently prepared by a process of oxidation. When it was established that oxymuriatic acid was an element, Davy called it chlorine on account of its colour.

Just as elements have been named after people and places, so have compounds. Glauber described a compound to which he gave the name 'miraculous salt', but it was subsequently called Glauber's salt. Now it is known as sodium sulphate-10-water. Another salt which has undergone several changes of name is Mohr's salt, commonly known as ferrous ammonium sulphate and named according to the latest rules as 'ammonium iron(II) sulphate(VI)–6–water'. Although the newest name is lengthy, it does permit the writing of the formula if the principles of the system are known; the formula is in fact $(NH_4)_2 Fe(SO_4)_2.6H_2O$. In spring water from Epsom, crystals were obtained which were given the name Epsom salt. These crystals are also called magnesium sulphate-7-water. The setting of broken bones makes use of plaster of Paris, a compound with the formula $2CaSO_4.H_2O$. Chile saltpetre comes from the rainless district of Chile and has the chemical name sodium nitrate.

Examples of the way in which compounds have been named could be multiplied over and over again. Some of the names still persist in common usage and will no doubt continue to do so whatever chemists decide about their system of nomenclature. Thus, the housewife is unlikely to refer to

sodium hydrogencarbonate, preferring to cook with bicarbonate of soda. Neither is she going to flavour her food with sodium chloride; salt has always served her purpose. Sometimes the common names cause confusion. Chalk is a naturally occurring form of the compound calcium carbonate (also occurring naturally as limestone). In the classroom, 'chalk' is used to write on the blackboard, but ordinary blackboard 'chalk' is made from gypsum — calcium sulphate-2-water. Another confusion is in the use of the word 'potash'. As a mineral this refers to potassium chloride, but to the chemist it is more likely to mean potassium hydroxide or potassium carbonate.

Enough has been written to indicate the need for some system to bring order out of the chaos of names given in a totally unorganised way. Some of the rules for naming compounds are simple in application and have already been followed in this book.

## 3. The modern system: names of binary compounds

The simplest type of compound is that formed between two elements. In naming these *binary compounds*, the ending '*-ide*' is used. The name of the compound is obtained by stating first the name of one of the elements, usually the more metallic one, and then adding the name of the second element, with its ending changed to *-ide*. Thus, the compound formed between magnesium and oxygen is called magnesium oxide. Magnesium is a metal and oxygen a non-metal, so the word oxygen is changed to *oxide* and this word follows magnesium in the name magnesium oxide. In the same way other binary compounds have the ending *sulphide, chloride, hydride*, and so on. The word hydride is normally only used for those compounds formed between metals and hydrogen. The non--metal hydrides usually have non-systematic (trivial) names — water, ammonia and methane have already been given as examples. Some pairs of elements form several different compounds which are distinguished by using a prefix. For example, carbon *mon*oxide $CO$ and carbon *di*oxide $CO_2$; sulphur *di*oxide $SO_2$ and sulphur *tri*oxide $SO_3$; *di*nitrogen oxide $N_2O$, nitrogen (mon)oxide $NO$ and nitrogen *di*oxide $NO_2$. These prefixes go on up to *octa* — as in, for example, osmium *octa*fluoride $OsF_8$.

Some metals form two oxides. It has been customary to make use of a suffix to the name of the metal in order to distinguish between the oxides. The suffix '*-ous*' is used for the compound containing the smaller amount of oxygen (or other non-metallic element), and the suffix '*-ic*' is used for the compound containing the larger amount of oxygen (or other non-metallic element). Often these suffixes are used with the Latin name of the element, rather than the English name. For example, iron (Latin name *ferrum*) forms two oxides $FeO$ and $Fe_2O_3$. According to the system these were named ferrous oxide and ferric oxide respectively. Since the formation of these different oxides is related to the variable valencies of the metals, the modern way to name these oxides takes this into account. Following the name of the metal, its valency is written in Roman numerals, and then oxide (or chloride, etc.) is written. Thus $FeO$ is iron (II) oxide and $Fe_2O_3$, is iron(III)oxide. In the preparation of oxygen, the catalyst was called manganese dioxide. Everyone understands that this name refers to $MnO_2$,

but to be consistent with the system the name should be manganese (IV) oxide. The oxides of manganese illustrate the limitations of using -ous and -ic. There are four oxides of manganese: $MnO$ — manganese (II) oxide, $Mn_2O_3$ — manganese (III) oxide, $MnO_2$ — manganese (IV) oxide, and $Mn_2O_7$ — manganese (VII) oxide.

While the names of all binary compounds end in '-ide', there is a group of compounds whose names end in -ide which are not binary compounds. We refer to the 'hydroxides'. Hydroxides contain three elements — a metal, oxygen and hydrogen. The oxygen and hydrogen are combined together to form a group of atoms known as the hydroxide (or hydroxyl) radical. So, if a formula such as KOH is encountered, it can be read simply as potassium hydroxide. If the name is given the formula can be written. For example, calcium hydroxide has the formula $Ca(OH)_2$ which can be obtained by applying the valency rules. Compare this with the use of the name 'slaked lime', which is the common name for the compound.

### 4. Naming acids and their salts

In the modern system of nomenclature, the names of all acids end in -ic, and the salts formed from them end in -ate with the exception of acids like hydrochloric acid. Hydrochloric acid gives salts which are binary compounds named as metal chlorides. In the modern system, if more than one acid is formed by the same elements, a Roman numeral at the end of the name helps to distinguish the different acids. However, because of the chemical theory involved in the application of the system, its use is not recommended in schools. The acids containing three elements — hydrogen, a second element, and oxygen — are named on the basis of the second element, with the ending '-ic' for the most common one. $H_2SO_4$ is sulphuric acid, and $HNO_3$ is nitric acid. With one oxygen atom fewer, the ending is changed to 'ous'. $H_2SO_3$ is sulphurous acid and $HNO_2$ is nitrous acid. This system is extended both for fewer oxygen atoms and for more oxygen atoms, but these details need not concern us here. In naming salts, those of the -ic acids are -ates, e.g. $Na_2SO_4$ is sodium sulphate. Salts of the -ous acids are -ites, e.g. $KNO_2$ is potassium nitrite.

Some acids have two or more atoms of available hydrogen and in salt formation this may not all be replaced. This is recognized by keeping hydrogen in the name of the salt. For example, $KHSO_4$ is called potassium hydrogensulphate. This will also be encountered under the name potassium bisulphate. The other common salts having similar names are the hydrogencarbonates and the hydrogensulphites; earlier, they were called bicarbonates and bisulphites. Notice that names like hydrogensulphate are written as one word, being the name of the radical $HSO_4$ which is to be treated as a single unit.

If a metal has more than one valency, then it will form different salts according to the valency it exhibits. As discussed earlier, two different valencies can be distinguished by adding -ous and -ic to the names and this is still the common way of naming these compounds. However, it is better to use the relevant Roman numeral after the name of the metal to show its valency as is done with the binary compounds. For example, $FeSO_4$ is iron(II) sulphate, and $Fe_2(SO_4)_3$ is iron(III)sulphate.

## 5. Naming hydrated compounds

Finally, if a compound crystallizes from solution with water of crystalliza-
tion, then the name of the crystalline compound should include a reference
to the presence of water. At an introductory stage, this can be done simply
by referring to the hydrated compound, e.g. hydrated copper sulphate
(strictly hydrated copper(II)sulphate, but copper (II) is so much more
common than copper (I) that normal reference to copper assumes it to be
copper (II) ). Already in this book the names of hydrates have been given
according to the systematic procedure, that is, the name of the anhydrous
compound is followed by a hyphen, a number giving the molecules of
water present, another hyphen, and the word 'water'. So, hydrated
copper sulphate becomes 'copper sulphate-5-water'. To show the lengths
which the modern system of nomenclature will go in the interests of clarity
and the desire to express as much as possible, the following full description
of the familiar blue crystals is given: tetraaquacopper(II)tetraoxosul-
phate(VI)-1-water.

A name is given to a substance so that it can be distinguished from other
substances. In the case of compounds, modern nomenclature also aims to
make it clear what elements are present and how the different atoms are
related to one another. The recognized authority on nomenclature is the
International Union of Pure and Applied Chemistry (IUPAC). Where
the modern system of naming has been mentioned, the reference is to the
system recommended by IUPAC. However, this system was designed to
help research chemists so it has been suitably modified for your use.

## Questions

1 · Give names to the following binary compounds: MgO, NaH, KCl,
   $CaH_2$, $Al_2O_3$, $SiO_2$, CaS, $Na_2O$, $Li_3N$, $AlF_3$. (Si — silicon, Li —
   lithium, F — fluorine).

2 The following pairs of elements form binary compounds in which
   the atoms of the two elements occur in equal numbers. Write
   formulas for them, and give names to them:

   a  Caesium (Cs) and fluorine (F)

   b  nitrogen and boron (B)

   c  oxygen and beryllium (Be)

   d  carbon and silicon (Si)

   e  aluminium and phosphorus (P)

   f  chlorine and fluorine.

3 What are the names of the following compounds (a) $KHCO_3$,
   (b) $Fe(OH)_3$, (c) FeS, (d) $NaHSO_3$, (e) $NaNO_2$?

4 Using prefixes to indicate the number of atoms of different kind,
   give names to the following binary compounds: $BF_3$, $SiO_2$, $PCl_5$, $SF_6$,
   $SiCl_4$.

5 Name the following: $K_2SO_4$, $Al_2(CO_3)_3$, $K_2SO_3$, $Al_4C_3$, $H_2SO_4$, $H_2S$, $PbO_2$.

6 Give the names of the compounds (a) $CaSO_4.2H_2O$
(b) $MgCl_2.6H_2O$ (c) $Na_2CO_3.H_2O$.

7 Give the formulas of the compounds (a) copper sulphate-5-water, (b) magnesium sulphate-7-water, (c) sodium carbonate-10-water.

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